

Orthodontic Materials

Scientific and Clinical Aspects

William A. Brantley
Theodore Eliades



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Scientific and Clinical Aspects

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To Drs. M. Max Sharpe and the late Dale B. Wade:
they showed the way, laid out the route, shared the thrill (T.E.)

To Vivian and my parents. (W.A.B.)

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Foreword

In this fast-changing world of orthodontic materia technica, the life cycle of many materials can be amazingly short. Too often we hear, "Oh yes, we used to use that!" The surge in improved bonding materials and the techniques, particularly, has been due to concentrated research, as have the new generation of archwires, brackets, and elastomeric ligatures. Even cements and impression materials have been subjected to searching analysis to improve their most desirable qualities.

This current compendium on the scientific and clinical aspects of orthodontic materials is edited by William Brantley and Theodore Eliades, with a supporting cast of international chapter authors.

Chapter 1 on structures and properties of orthodontic materials by William Brantley not only reports his ongoing research, but definitive work of other material scientists. Atomic and interatomic arrangements in metallic, ceramic, and polymeric materials are presented in a concise and understandable fashion.

William Brantley teams up with co-editor Theodore Eliades and Alan Litsky on Mechanics and Mechanical Testing of Orthodontic Materials for Chapter 2. Bending and torsional deformation, so important to orthodontic manipulation, fatigue properties, and bond strength tests are part of a potpourri of materia technica covered. This is again quite readable for the average clinician and has direct clinical practice application.

Chapter 3, by George Eliades and William Brantley, addresses instrumental techniques for the study of orthodontic materials. This is a "first" in any orthodontic text. Scientific principles and experimental procedures are presented for a variety of laboratory analyses.

Chapter 4 on orthodontic wires and their alloys is a major assignment, and William Brantley accepts the daunting challenge.

Enamel etching and bond strength are of course vital to successful, non-iatrogenic bonding of attachments and are authored by John Powers and Marion Messersmith in Chapter 5.

Chapter 6 by Bjørn Øgaard covers the role of oral microbiota, the oral microbiological changes, long-term enamel alterations due to decalcification and caries prophylactic aspects. State of the art diagnostic methods are presented.

Orthodontic brackets coverage is a major challenge, because of the multiplicity of bracket designs and brackets, and the frequent advances being made for easier, safer bonding. This challenge is accepted in Chapter 7 by a threesome-

Theodore and George Eliades and William Brantley.

Chapter 8 on elastomeric ligatures is again multi-authored. Recent evidence of structural alterations during use is discussed by Theodore and George Eliades, David Watts and William Brantley.

Chapter 9 on orthodontic adhesive resins and composites and principles of adhesion is authored by David Watts.

Closely related to Chapter 9 is Chapter 10, which presents chemically cured, light-cured, and dual-cured adhesive systems, together with recently introduced moisture-active adhesives. Again it is authored by the Eliades team.

Chapter 11 is closely allied to the two previous chapters, and covers traditional cements used in bonding, as well as compomers and glass-ionomer cements. It is authored by Aphrodite Kakaboura and George Vougiouklakis.

In Chapter 12 impression materials are covered from an orthodontic perspective by William Johnston. The emphasis is on alginates.

Chapter 13 discusses bonding to non-conventional surfaces (e.g., amalgam, gold, porcelain). It is authored by Efstratios Papazoglou.

Vital to all oral materia technica are biocompatibility and cytotoxicity of the materials used. Chapter 14 by John Wataha addresses this major challenge.

The final chapter in the book, Chapter 15, is closely related to Chapter 14 and is badly needed in this litigious world. This again is presented by an international team, Arne Hensten-Pettersen, Nils Jacobsen, and Margrét Rósa Grímsdóttir on a vital subject-allergic reactions and safety concerns.

A convenient appendix on the names and addresses of orthodontic materials' manufacturers makes it easy for the reader to make immediate use of the research studies reported.

It is a pleasure to write a preface for another Thieme book. Thieme means quality personified – and is a role model for orthodontic publishers. Rakosi, Jonas, and Graber's *Atlas on Orthodontic Diagnosis*, published by Thieme, is available in six languages. I anticipate similar success for this opus.

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Preface

Seminars or courses on clinically relevant materials have been a component of graduate orthodontic education for several decades. Originally, students received instruction in the scientific principles and proper manipulation for the relatively small number of dental materials used in clinical practice. Major subject areas were archwires and stainless steel brackets, elastics and elastomerics, alginate impression material, zinc phosphate cement, and acid-etching of enamel and adhesive bonding of brackets. Technological developments over the past two decades have led to the introduction of a plethora of new orthodontic products at a dramatically increasing rate, necessitating more comprehensive training in the field of dental materials science. The further progression of materials development has resulted in additional new products that are significant advances from their predecessors (e.g., Copper Ni-Ti archwires and compomer adhesives). Accordingly, the teaching format for this discipline has had to expand to encompass a much wider variety of materials.

While the educational format in the United States varies substantially among teaching philosophies, the graduate orthodontic curriculum typically contains one to two credit hours devoted exclusively to orthodontic materials over a single quarter or semester. This level of educational experience is mandated by the Accreditation Standards that have been developed by the American Dental Association for Advanced Specialty Education Programs in Orthodontics and Dentofacial Orthopedics. The seminar or course in orthodontic materials is generally complemented by courses in the biomechanics of tooth movement, and is taken by graduate students during their first or second year of specialty training.

A modern book on orthodontic materials should include the following topics: an introduction to the concepts of materials science; study of the composition, structure, and properties of specific orthodontic materials used in clinical practice; interactions of orthodontic materials with other dental materials and dental hard tissues in the oral cavity; and the issues of biocompatibility, cytotoxicity, and allergic reactions for both patients and operators. This background should permit the orthodontist to make rational material selections for efficient treatment mechanics and to appreciate the complex effects of the oral environment on orthodontic materials. Moreover, it is essential for a textbook to integrate the dental ma-

terials science aspects with the clinical manipulation and use of these materials.

In the absence of a textbook, courses or seminars in orthodontic materials have often been taught on a literature review basis, using relevant published articles that might be supplemented by lecture notes. From an academic perspective, this teaching approach is inverted, since literature review sessions should follow development by students of the required background, which is traditionally achieved through formal textbook-driven education. This approach appears to have led frequently to the establishment of empirical performance criteria, which were usually derived from the clinical experience of individuals who served as consultants for the orthodontic materials industry.

Additionally, the lack of a focused textbook source of information has hindered the research efforts of graduate students in orthodontics and dental materials who undertake MS thesis and PhD dissertation projects in the field of orthodontic materials. As previously noted, the field of orthodontic materials has greatly expanded, with the introduction of new materials for archwires, auxiliaries, adhesives, elastomerics, cements, and other applications. Within each group of these materials, there is frequently a bewildering array of products with different properties. A noteworthy example is the wide spectrum of orthodontic adhesives that have quite different setting mechanisms and properties. Concurrently, the study of orthodontic materials has become much more complex owing to the availability of new, relatively sophisticated instrumentation.

The previous lack of an orthodontic materials textbook derives from the limited number of types of orthodontic materials available in the past, along with the traditional emphasis in the graduate curriculum on various treatment modalities and the related orthodontic mechanics. With the latest advances in technology, the former is no longer the case, while the latter point must be reconsidered since modern orthodontic mechanics can be greatly affected by the choice of materials used. For example, while often mistakenly overemphasized, selection of orthodontic archwire alloys possessing specific mechanical properties may alter the duration of therapy.

The enormous changes in orthodontic treatment mechanics, treatment duration, and appliance efficiency due to improvement in materials are perhaps the most prominent differences that

distinguish contemporary orthodontic practice from the way Dr. Angle was practicing at the dawn of the development of the specialty. Although our knowledge about the sequence of biological events leading to tooth movement and craniofacial adaptation has been improved substantially, the basic concepts of treatment mechanics have not essentially changed. However, materials are now available that generally allow the application of forces of a known magnitude, direction, and duration, in a predictable manner and with minimum substrate alterations induced. No other contribution appears to have made such a change in the way the profession is being practiced as has the development of modern orthodontic materials.

The development of an array of distinctively different materials has necessarily modified the teaching methodology for the orthodontic materials course in the majority of the graduate orthodontic programs. Teaching methods have evolved from a "manual concept," which was limited to the description of proper materials manipulation on a subject-driven basis, to the formulation of a principle-based approach involving materials science. The latter has given rise to the requirement for a more organized teaching method, of which an essential adjunct would be the availability of a suitable textbook.

We hope that the scope of this book provides the background needed for the comprehensive study of orthodontic materials, and that students and faculty will find this book useful in efficiently organizing their research and teaching activities, respectively. Portions of this book are based upon a course in orthodontic materials that one of us (W.A.B.) has taught for over two decades, first at the Marquette University School of Dentistry and for the past decade at the College of Dentistry of The Ohio State University. Numerous graduate students at both institutions will find citations to their thesis or dissertation research in several chapters. During these two decades, many individuals contributed greatly to the tremendous advancements that have occurred in the field of orthodontic materials. Individuals (other than contributors to this book) who should be cited for their substantial body of significant work include George Andreasen, Samir Bishara, Charles Burstone, Jon Goldberg, Robert Kusy, Fujio Miura, Ram Nanda, and Robert Nikolai. There is certainly also a lengthy list of other researchers who have published highly important articles in the orthodontic materials literature over the past two decades.

We are most grateful to our contributors from the United States and Europe for their collaboration in preparing this book, and to Clifford Bergman, Gabriele Kuhn, and Gert Krüger (Thieme, Stuttgart) for undertaking the publication of such a demanding project.

September 2000

*William A. Brantley
Theodore Eliades*

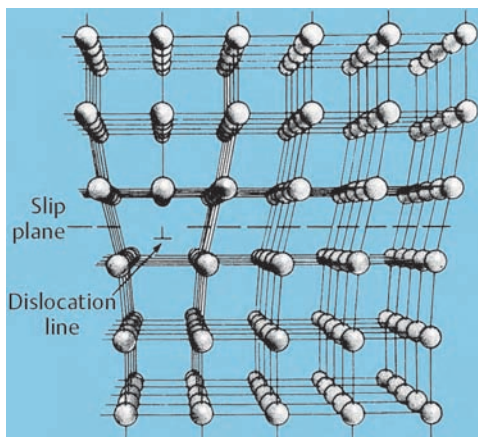
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1 Structures and Properties of Orthodontic Materials

William A. Brantley



Schematic illustration of an edge dislocation in a crystalline material

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Introduction

Knowledge of fundamental principles governing the relationships between compositions, structures and properties is central to an understanding of orthodontic materials. Because wide arrays of metallic, ceramic, and polymeric materials are used in the profession, and new materials are continuously being introduced, it is essential that the scientific basis for the selection and proper use of materials for clinical practice be thoroughly understood.

The general plan of this chapter is to develop these concepts following the standard basic approach that has historically been used in engineering materials science. First, the different modes of interatomic bonding will be described, followed by a description of how these modes of bonding lead to the atomic arrangements found in the metallic, ceramic, and polymeric materials. Second, terminology will be presented to describe the clinically relevant

properties of these orthodontic materials. After these foundations have been acquired, the linkages between the structures and properties of these materials can readily be understood.

It is expected that graduate students in orthodontic programs, as well as practicing orthodontists, will already have been exposed to many of these concepts in an introductory biomaterials course or a series of lectures that are found in the predoctoral dental school curriculum. Because of the very wide scope of the subject matter involved, it is not possible in a single chapter to fully develop all of the topics germane to the structure-property relationships of orthodontic materials. The reader is referred to the excellent textbooks on dental materials science and engineering materials science listed at the end of this chapter for further information.

Interatomic Bonding and Atomic Arrangement

Modes of Interatomic Bonding

Traditionally, textbooks on dental materials science have subdivided the modes of interatomic bonding into two major categories: chemical bonding and physical bonding. Chemical bonding involves the valence electrons of atoms that participate in chemical reactions and includes the three modes of covalent, ionic, and metallic bonding. Physical bonding, also known as van der Waals bonding, occurs between atoms or molecules with closed electronic shells.

Covalent bonding involves the sharing of valence electrons, such as that which occurs for carbon-carbon bonding in polymer chains. Another example is the sharing of valence electrons between silicon and oxygen to form SiO_2 . In both of these examples, after the sharing of valence electrons the atoms have the closed shell or noble gas electron configurations. The strongest covalent bonding occurs with the carbon atoms in diamond, where each of the four valence electrons (two $2s$ and two $2p$) for a given carbon atom is shared with a valence electron of an adjacent carbon atom in a hybridized sp^3 arrangement. Covalent

bonding is highly directional, and materials dominated by covalent bonding typically have relatively open structures and low densities, and also lack the ability to undergo permanent deformation except at high temperatures.

Ionic bonding involves a transfer of valence electrons, such as that which occurs between sodium and chlorine atoms to form the NaCl molecule. The sodium atom has a single $3s$ electron in the M shell and the chlorine atom has a single $3p$ vacancy in the M shell (Table 1.1). Transfer of the valence electron from the sodium to the chlorine atom allows both atom species to have the closed shell noble gas configuration, and the bonding arises from the strong electrostatic attraction between the resulting positive and negative ions. Because of the symmetric electron charge distributions around the ions, ionic bonding is not directional. Materials dominated by ionic bonding tend to have higher densities than materials dominated by covalent bonding.

Generally, materials that are dominated by covalent or ionic bonding should be considered to have a mixture of both modes of interatomic bonding. Pauling developed an empirical

Table 1.1 Electronic configurations for some atoms

Element	Atomic Number	Electronic Configuration
C	6	$1s^2 2s^2 2p^2$
O	8	$1s^2 2s^2 2p^4$
Na	11	$1s^2 2s^2 2p^6 3s^1$
Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Ag	47	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$
Au	79	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$

concept, in which the fractional ionic bonding character for simple materials consisting of two different atomic species is related to the difference in electronegativity of the two atoms. The electronegativity for a given atom is approximately proportional to the sum of the ionization potential and the electron affinity. For example, from a plot of the electronegativities for the different atoms, it can be estimated that the fractional ionic character is 0.52 and 0.63 for SiO_2 and Al_2O_3 , respectively.

In metals the valence electrons are loosely bound and can be considered to form a gas that permeates the atomic arrangement of the resulting ionic cores, in contrast to the localization of valence electrons around parent atoms for covalent and ionic bonding. Metallic bonding is nondirectional on the atomic scale, and the metallic atoms form arrangements leading to materials of high density. Table 1.1 shows the electronic configurations for the atoms of some metals that are found in orthodontic and restorative alloys. The valence electrons that are lost in forming the cations from these metals are obvious. Many of the metals listed in Table 1.1 are transition elements, in which the outermost subshells (4s, 5s, 6s or 7s) are filled before the interior subshells. Transition metals frequently have multiple

valences and are important for orthodontic and restorative alloys.

Physical interatomic bonding occurs with symmetric atoms (noble gas atoms) or molecules, such as methane (CH_4), where weak dispersive forces arise from fluctuations in the electronic charge distribution. This bonding mode can have significance for the adhesion between different materials where a polymeric material is involved. The other type of physical bonding occurs with asymmetric molecules having permanent dipole moments, such as water (H_2O), where strong electrostatic forces exist between the positive and negative centers of charge.

Atomic Arrangements for Metallic Materials

In general, materials can be subdivided into two categories according to their atomic arrangements. In crystalline materials there is a three-dimensional periodic pattern of the atoms, whereas no such long-range periodicity is present in noncrystalline materials, which possess only short-range atomic order.

It is appropriate to first consider the pure metals, which have the simplest compositions (a single element) and atomic arrangements.

Table 1.2 The seven crystal systems

System	Axial Lengths	Axial Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a_1 = a_2 = a_3 \neq c$	$\alpha_1 = \alpha_2 = \alpha_3 = 120^\circ; \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

The axial lengths (a , b and c) are the atomic repeat distances or lattice parameters along the three crystallographic axes, except for the hexagonal system where the axial lengths (a_1 , a_2 and a_3) in the basal plane are used.

For crystal systems other than hexagonal, the axial angle α is the angle between the b and c axes, and the β and γ angles have analogous definitions. In some textbooks the rhombohedral system is referred to as the trigonal system.

The three identical axial angles in the basal plane of the hexagonal system are designated α_1 , α_2 , and α_3 . γ is the angle between each of the three axes in the basal plane and the axis in the c -direction

Except for extraordinary conditions of preparation (solidification from the liquid state or condensation from the vapor state under extremely rapid conditions) that are not applicable to dental alloys, metals always have crystalline structures. There are seven crystal systems (cubic, tetragonal, orthorhombic, rhombohedral [trigonal], hexagonal, monoclinic, and triclinic), with lattice parameters as summarized

in Table 1.2. The corresponding fourteen space lattices (Bravais lattices) are listed in Table 1.3. Inherently, a space lattice is a geometric construct wherein each point has identical surroundings. Crystal structures of real materials are based upon space lattices, where there is a single atom or a group of atoms at each space lattice point.

It is most convenient to visualize the crystal structures of metals in terms of their unit cells, where a unit cell is the smallest portion that can be repeated in three dimensions to produce the crystal structure. Figure 1.1 shows the unit cells of the important body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) structures for metals in dentistry. For comparison, the unit cell for the simple cubic structure is also shown. The hcp structure can be considered as formed from two interpenetrating simple hexagonal structures. Important pure metals found in orthodontic alloys for archwires (Chapter 4) and brackets (Chapter 7) that have these crystal structures are as follows:

fcc Fe (above $\sim 910^\circ\text{C}$), Ni
 bcc Fe (below $\sim 910^\circ\text{C}$ and above $\sim 1400^\circ\text{C}$),
 Cr, Ti (above $\sim 880^\circ\text{C}$)
 hcp Co, Ti (below $\sim 880^\circ\text{C}$).

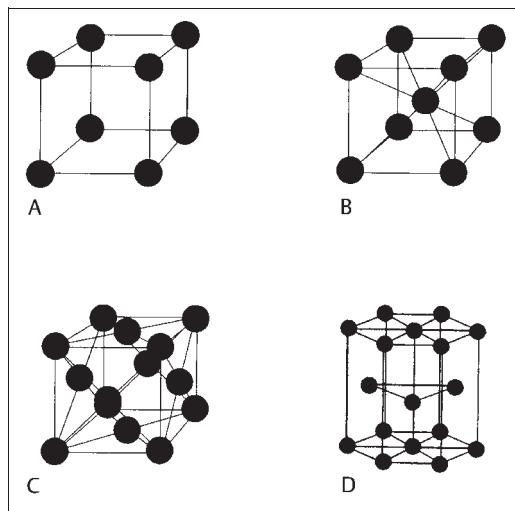


Fig. 1.1 Unit cells for the simple cubic (A), body-centered cubic (B), face-centered cubic (C), and hexagonal close-packed (D) structures. (Adapted from Anusavice, 1996)

It can be seen that, while nickel and chromium have the fcc and bcc structures, respectively, at all temperatures below their melting

Table 1.3 The fourteen space (Bravais) lattices

Crystal System	Space Lattice
Cubic	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Simple tetragonal Body-centered tetragonal
Orthorhombic	Simple orthorhombic Body-centered orthorhombic Face-centered orthorhombic Base-centered orthorhombic
Rhombohedral (Trigonal)	Simple rhombohedral
Hexagonal	Simple hexagonal
Monoclinic	Simple monoclinic Base-centered monoclinic
Triclinic	Simple triclinic

In textbooks on crystallography, the term *simple* is replaced by the term *primitive*

points, iron and titanium have crystal structures that depend upon temperature. For example, titanium has the hcp α structure from room temperature up to $\sim 880^\circ\text{C}$, where there is a transformation to the bcc β structure. At room temperature iron has the bcc α structure

and transforms to the fcc γ structure at $\sim 910^\circ\text{C}$. The different crystal structures of a given metal (or other crystalline material) are termed polymorphic or allotropic forms. Cobalt ordinarily has the hcp α structure but can also exist in an fcc β polymorphic form.

Atomic Arrangements for Ceramic Materials

Ceramics, which consist of more than one atomic species, can have crystalline or noncrystalline structures, depending upon the material and sometimes the mode of preparation. Important ceramics for orthodontic applications are aluminum oxide (alumina) and zirconium oxide (zirconia), which are used as bracket materials (Chapter 7). Other ceramics are found in the powder portions of cements (Chapter 11). Silicon dioxide (silica) is an important filler in composite restorative resins.

The crystal structure of aluminum oxide is illustrative of the principles involved with ceramics having substantial ionic bonding character. The crystal structure consists of a nearly hcp arrangement of the larger oxygen anions (O^{2-}), with the smaller aluminum cations (Al^{3+}) located in two-thirds of the octahedral interstitial sites in the hcp structure (Fig.1.2).

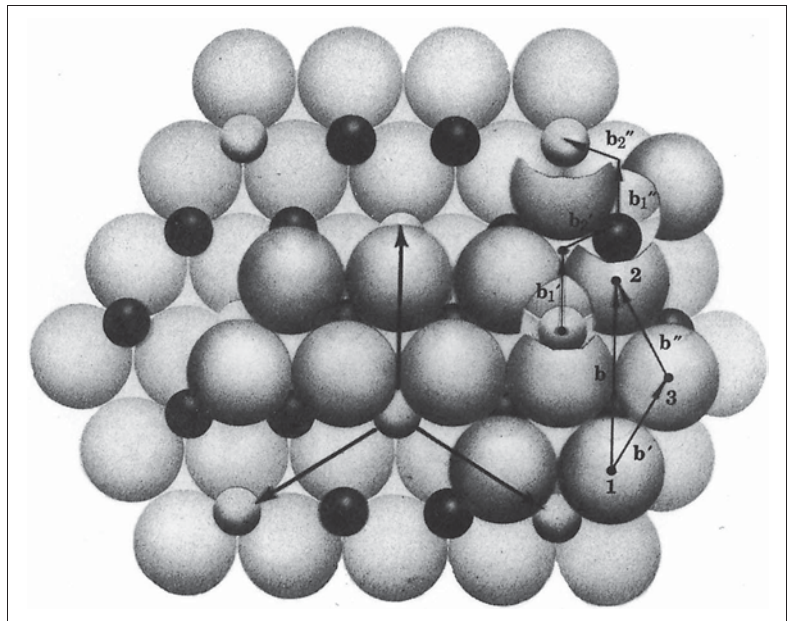


Fig. 1.2 Structure of alumina.
(From Kingery *et al*, 1976)

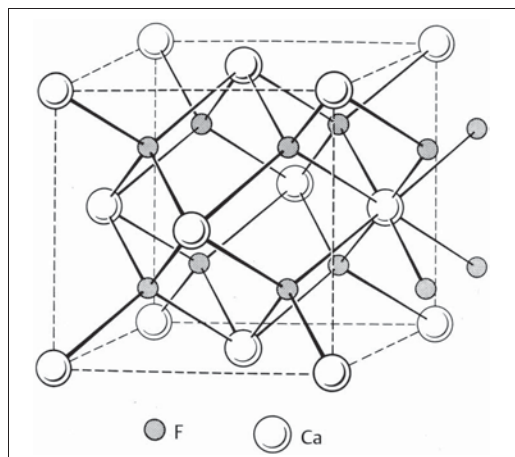


Fig. 1.3 Structure of calcium fluoride (CaF_2), which is similar to the structure of zirconia. (From Kingery *et al*, 1976)

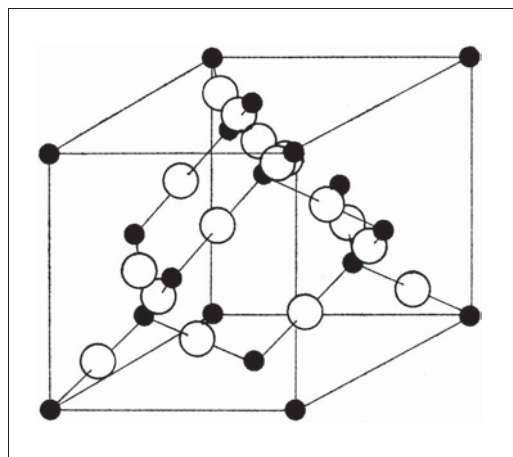


Fig. 1.4 Structure of cristobalite. (From Greener *et al*, 1972)

The layers in the structure provide the maximum separation of the Al^{3+} ions. These octahedral sites have six-fold coordination, *i.e.*, each aluminum ion is surrounded by six oxygen ions. The crystal structure is determined by the ratio of the radii of the aluminum and oxygen ions and the requirement of an electrically neutral unit cell. The crystal structure of zirconia at room temperature consists of a distorted simple cubic (monoclinic) arrangement of the oxygen ions, with the zirconium cations (Zr^{4+}) located in half of the available sites (eightfold coordination), similar to Figure 1.3.

Silica is principally found in dental materials (investments, composite resins, and elastomeric impression materials) in the crystalline quartz or cristobalite polymorphic forms or as the glassy form of vitreous silica. Moreover, both cristobalite and quartz have high-temperature (the more stable form) and low-temperature polymorphic forms. The basic unit in the structure of SiO_2 is the SiO_4 tetrahedron, where the small Si^{4+} cation is bonded to four much larger O^{2-} anions in a tetrahedral arrangement. The high-temperature form of cristobalite (Fig. 1.4) has a diamond cubic (the structure for the diamond form of carbon) arrangement of the SiO_4 tetrahedra. The high-temperature form of quartz has a complex structure consisting of connected chains of SiO_4 tetrahedra. A schematic illustration of the structure of crystalline SiO_2 in two dimensions is provided in Figure 1.5.

The structure of fused or vitreous silica has the short-range order of the silicon and oxygen ions shown in Figure 1.5 but lacks the long-range periodicity found in crystalline materials. For feldspathic dental porcelain, where glass-modifying or fluxing oxides such as Na_2O ,

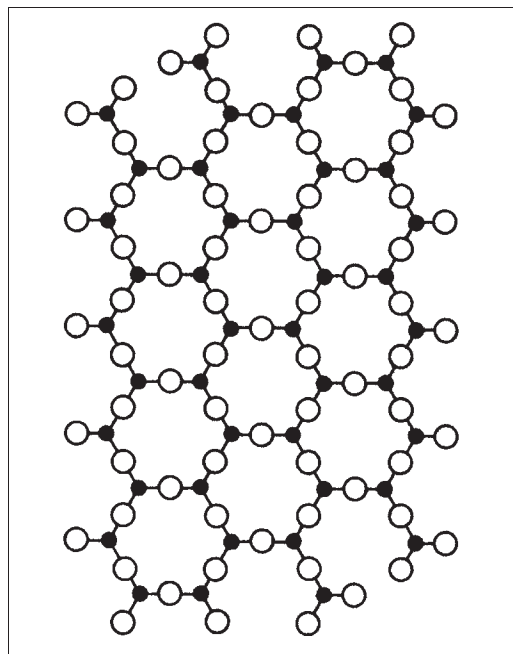


Fig. 1.5 Two-dimensional illustration of the structure of quartz. (From Kingery *et al*, 1976)

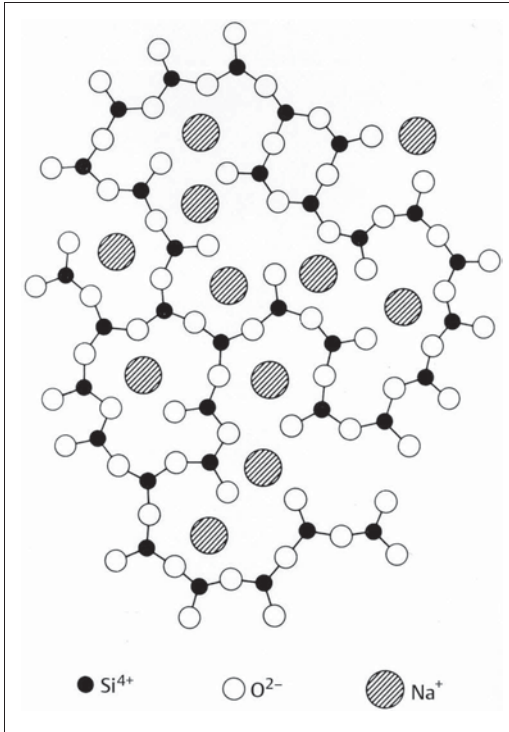


Fig. 1.6 Structure of feldspathic dental porcelain, showing typical locations of glass-modifying cations and nonbridging oxygen ions. (From Kingery *et al.*, 1976)

K_2O , and CaO are added to SiO_2 , the Na^+ , K^+ , and Ca^{2+} ions disrupt the three-dimensional silicate framework structure. Nonbridging oxygen ions that do not connect Si^{4+} ions are created by these large cations, which are situated in open spaces in the structure (Fig. 1.6).

Atomic Arrangements for Polymeric Materials

A variety of polymeric materials are used in orthodontics, such as elastomeric impression materials (Chapter 12) and polyurethane modules for tooth movement (Chapter 8), adhesive cements for bonding brackets to enamel (Chapter 10), and polycarbonate brackets (Chapter 7). All of these polymeric materials are based upon macromolecules with varying compositions, molecular weights, and degrees of cross-linking. The general structures of a polyurethane elastomer for tooth movement and

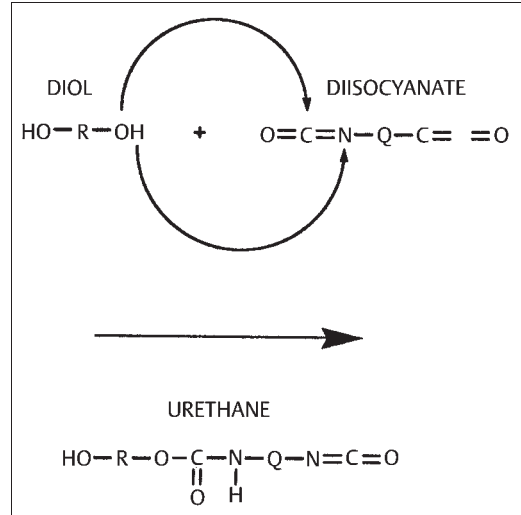


Fig. 1.7 General structure of a urethane group (OCONH) formed by the reaction of a diol and a diisocyanate. (From Anusavice, 1996)

an alginate impression material are shown in Figures 1.7 and 1.8, respectively. The polymers have predominantly noncrystalline structures without long-range periodicity. Illustrations of important structural components for adhesive resins will be shown in Chapter 10. Information on the structure of polymeric materials is presented in references listed at the end of this chapter.

The elastomeric materials are lightly cross-linked and undergo a glass transition below room temperature. Below the glass transition temperature, the elastomers are relatively rigid, whereas above the glass transition temperature these materials become highly flexible with thermal activation of the polymeric backbones and side chains. The elastomers also typically contain a second phase of polymer crystallites, which undergo melting at temperatures above the glass transition temperature. In contrast, the polycarbonate material used for brackets is highly cross-linked and relatively rigid, although these brackets are subject to problematic deformation under the clinical loading imposed by archwires.

Mechanisms for permanent deformation of polymeric materials include chain stretching, slippage between adjacent chains, and chain scission. There is no mechanism on the molecular level in the noncrystalline orthodontic

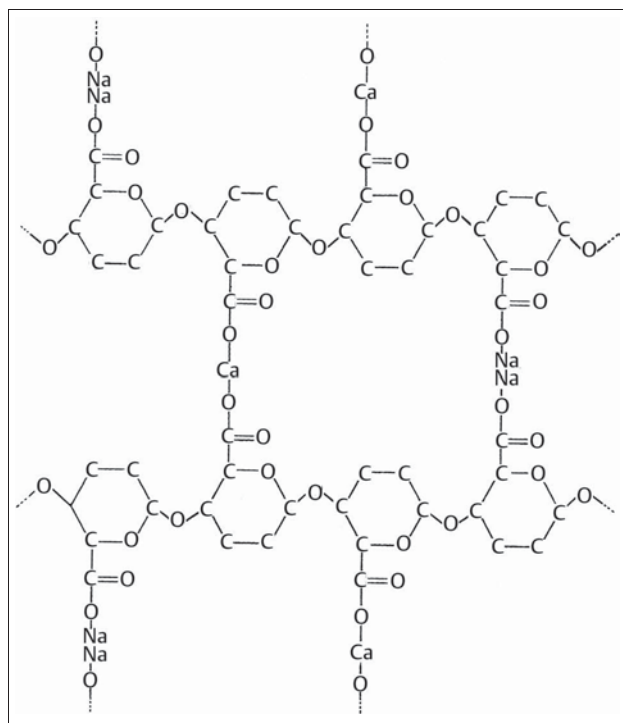


Fig. 1.8 Schematic polymer structure of alginate impression material in which sodium alginate molecules have cross-linked to form calcium alginate (Chapter 12). (From Anusavice, 1996)

polymers that is analogous to the dislocation motion or twinning that occur in crystalline metals. Consequently, the cross-linked adhesive resins and the polycarbonate brackets fail in a brittle manner, although slow, time-depen-

dent creep deformation under static loads may be possible. Under normal loading conditions, these brittle polymers will fail by propagation of cracks from microstructural flaws, analogously to the situation for ceramics.

Properties of Orthodontic Materials

Property Areas of Importance for Orthodontic Materials

The clinically important property areas for orthodontic materials include mechanical and surface properties for a variety of materials, and the corrosion properties for archwire alloys. The purpose of this section is to introduce property terminology that will be germane to the subject matter presented in subsequent sections of this chapter and that will provide a background for understanding the properties of the different types of orthodontic materials discussed in Chapters 4 to 15.

While thermal and optical properties are highly important for restorative dental materi-

als, these areas have been omitted from this section. Little work has been reported on the roles of thermal properties for orthodontic materials, and the importance of optical properties for the clinical performance of ceramic orthodontic brackets will be discussed in Chapter 7.

Mechanical Property Concepts for Orthodontic Materials

A material specimen can be subjected to three basic modes of force or load application, as shown in Figure 1.9. (A force is considered to be a vector quantity with both magnitude

and direction, whereas a load is generally considered to have some magnitude only without any direction being specified.) A tensile force causes an elongation in the direction of load application, whereas a compressive force causes a contraction in the direction of load application. A shear force causes either a sliding displacement of one side of a specimen with respect to the opposite side or a twisting about the specimen axis (termed torsion).

The force or load application causes an internal resisting force in the material or stress (σ) due to the displacement of the atoms. The engineering or nominal stress customarily used for orthodontic materials is given by the quotient of the applied force and the original cross-sectional area ($\sigma = F/A_0$). Consequently, stress can be considered as applied force intensity or, equivalently, the internal force intensity resisting the applied force. In the metric or *Système International* (SI) system, the usual unit of stress is the megapascal (MPa), where $1 \text{ MPa} = 10^6 \text{ N/m}^2 = 1 \text{ N/mm}^2$, since $1 \text{ Pa (pascal)} = 1 \text{ N/m}^2$ represents a very small value of stress. A useful relationship for comparing the results in newer publications with older articles having the English system of units is that $1 \text{ MPa} = 145 \text{ psi}$ (pounds per square inch).

The force application concurrently causes strain (ϵ), *i.e.*, a change in dimensions of the material specimen. For the tensile or compressive loading typically performed in the research laboratory, the engineering or nominal strain (which is customarily used for orthodontic materials) is given by the quotient of the change in length and the original reference or gauge length, *i.e.*, $\epsilon = \Delta l/l_0$. For engineering shear strain, $\tan \theta = al/h$, where θ is the angle of inclination after shear loading, al is the displacement in the direction of shear loading, and h is the specimen height in the direction perpendicular to the shear loading. For the usual situation where the shear strain is very small, $\tan \theta \approx \theta$, with the angle (θ) given in radians ($1 \text{ rad} = 180/\pi \text{ deg}$).

An axial stress (either tensile or compressive) on a specimen will result in a transverse strain (ϵ_2) of opposite sense to the main axial strain (ϵ_1). For example, an axial tensile stress on a rod-shaped specimen will induce a lateral contraction in addition to the tensile strain along the axis. Poisson's ratio (ν) is defined by the re-

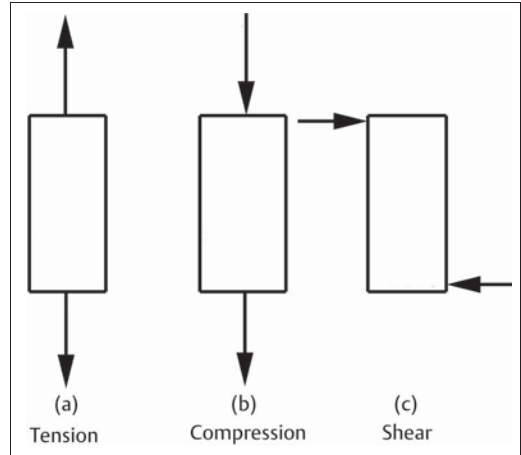


Fig. 1.9 Three basic modes of load application. (Adapted from Greener *et al*, 1972)

lationship $\nu = -\epsilon_2/\epsilon_1$, where the negative sign is used to yield a positive value for ν (typically about 0.2–0.3 for most dental materials).

For relatively small loads, the stress is below the elastic limit of the material, and reversible elastic strain occurs that disappears completely when the specimen is unloaded. When the stress reaches a sufficiently high value, a ductile material begins to undergo irreversible plastic or permanent deformation, whereas a brittle material will fracture without any significant permanent deformation. The permanent deformation of a ductile material will continue with increasing stress until fracture takes place.

This behavior can be portrayed by the familiar engineering stress-strain plot, which is illustrated for the tensile loading of a ductile metal specimen in Figure 1.10. This plot contains an initial linear region that corresponds to elastic deformation, followed by a curved region corresponding to permanent deformation and work hardening that terminates when the metal fractures.

The stress at the end of the linear region is termed the proportional limit (PL). For values of stress exceeding the PL, the strain is no longer proportional to stress. The slope of the initial linear region is the modulus of elasticity (E), which corresponds to the elastic stiffness or rigidity of the material, *i.e.*, the amount of stress required for unit strain. Hence, $E = \sigma/\epsilon$, where σ does not exceed the PL (also termed Hookean elasticity). The elastic modulus is generally

reported in gigapascals (GPa) where $1 \text{ GPa} = 10^9 \text{ N/m}^2 = 10^3 \text{ MPa} = 145,000 \text{ psi}$. Values of elastic modulus for orthodontic archwire alloys are provided in Chapter 4.

For elastic shear loading, the stress and strain are related by the shear modulus (G). With homogeneous (properties independent of position) and isotropic (properties independent of direction) materials, there are only two independent elastic constants. For such materials, the values of Young's modulus, shear modulus, and Poisson's ratio are related by the expression

$$E = \frac{G}{2(1 + \nu)}$$

While most metallic and ceramic dental materials can be considered homogeneous and isotropic, an archwire will have different mechanical properties in directions parallel and perpendicular to the axis because of the wire drawing.

An important mechanical property for orthodontic alloys is the modulus of resilience, or resilience, which is the area of the stress-strain plot up to the PL. The modulus of resilience represents the energy per unit volume required to load a specimen of the alloy to the end of the elastic range and is equivalent to the biomechanical spring energy of the alloy. Since this area on the stress-strain plot is a right triangle, it follows that the modulus of resilience is given by $(\text{PL})^2/2E$.

The proportional limit is determined by placing a straightedge on the stress-strain

plot, and the elastic limit is determined with the aid of precise strain measurement apparatus in the laboratory. While these two properties thus do not have the same value for an alloy, many investigators and textbooks treat the two terms as synonymous. Because there is some degree of subjectivity in determining the value of the PL, the yield strength (YS) is generally used for designating the onset of permanent deformation. Conventionally, the 0.1% YS is reported, which represents the value of stress corresponding to 0.1% permanent strain. The 0.1% YS is determined by the intersection of the curved portion of the stress-strain plot with a construction line that begins at the position of 0.1% strain on the horizontal axis and is parallel to the linear portion of the stress-strain plot (Fig. 1.10). Some investigators report the yield strength for 0.2% or 0.5% permanent strain (which will be higher than the 0.1% offset yield strength), so it is essential that the very small amount of permanent deformation used for the determination of YS be specified. Values of the 0.1% offset yield strength for archwire alloys are provided in Chapter 4.

The maximum point on the stress-strain plot for tensile loading is called the ultimate tensile strength (UTS), or simply the tensile strength or strength. With compressive loading, the corresponding maximum stress is called the compressive strength. For relatively brittle materials, the tensile strength or compressive strength corresponds to the stress at fracture. However, the nominal stress will decrease after the UTS for materials with substantial ductility, as the test specimen undergoes substantial necking down (decreasing cross-sectional area) within the gauge section.

Figure 1.10 shows the unloading behavior that would also be observed for the tension test of an archwire alloy (such as stainless steel, cobalt-chromium-nickel and β -titanium) displaying standard linear elasticity (Chapter 4), where the path of unloading is parallel to the initial linear portion of the stress-strain plot. (The unloading path is designated on Fig. 1.10 as the line for ductility.) The loading and unloading behavior for the nickel-titanium archwire alloys that display nonlinear elasticity will be discussed in Chapter 4. In principle, the relevant stress-strain behavior for an archwire alloy would always be the unloading plot rather than the loading plot.

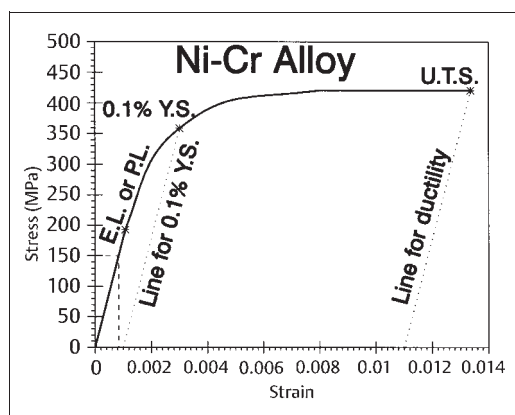


Fig. 1.10 Tensile stress-strain curve for a ductile nickel-chromium dental alloy exhibiting linear elasticity. (Illustration prepared by Dr. William M. Johnston)

A highly important clinical property for archwire alloys is the springback after the maximal elastic deflection, which would be given by PL/E in Figure 1.10. However, since clinicians may activate archwires slightly into the permanent deformation range, a more practical expression of YS/E is given for springback in the orthodontic literature. In a similar manner, some investigators use the expression $(YS)^2/2E$ to determine a more practical value for the modulus of resilience.

In Figure 1.10, the intersection of the line for unloading with the horizontal axis corresponds to the amount of permanent deformation that had taken place just before the unloading occurred. This permanent deformation is termed the percentage elongation, given by the expression $[(l_f - l_0)/l_0] \times 100\%$ where l_f is the final specimen length before unloading. However, permanent deformation (termed ductility for tensile loading) has little significance for orthodontic alloys, where the focus is on elastic deformation and force delivery. For prosthodontic and implant alloy test specimens, which typically have diameters of 3 mm or similar dimensions, the ductility is determined by fitting together the fractured specimen segments and carefully measuring the permanent increase in the original gauge length.

For brittle orthodontic materials, such as cements, the diametral compression test may be performed to obtain the tensile strength. This test is particularly convenient because small disk specimens can be used. The loading mode is shown in Figure 1.11, where the vertical compression causes tensile strain in the lateral direction. The specimen undergoes fracture along the indicated midline; in the case of triple-cleft fracture, each of the fractured specimen halves further fractures into two pieces. This test is discussed further in Chapter 3.

Only a few hardness measurements for archwire alloys have been reported in the orthodontic materials literature (Chapter 4), where the Knoop and Vickers indentation techniques have been employed. Both of these microhardness tests use a diamond indenter to apply a known load to the surface of a metallurgically polished specimen. After the dimensions of the indentation are measured microscopically (Fig. 1.12), the Knoop or Vickers hardness number can readily be found from published tables. The Vickers technique uses a pyramidal

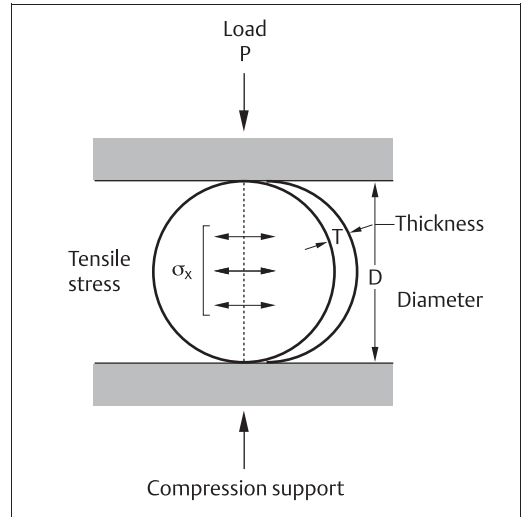


Fig. 1.11 Loading mode for the diametral compression test. (From Craig, 1997)

indenter with a square base, and the lengths of the two diagonals of the surface indentation are averaged for each measurement. The Knoop indenter is specially cut so that the recovery of elastic deformation upon unloading takes place only along the short diagonal of the diamond-shaped indentation, and the length of the long diagonal is measured.

Viscoelastic properties are highly important for both impression materials and elastomeric modules. For these materials, the rate and duration of loading can have significant influences on mechanical properties, in contrast to the lack of dependence typically found for metals and ceramics with the usual rates of loading in the laboratory. A schematic plot is shown in Figure 1.13 for a viscoelastic material that is subjected to a constant load in tension for a period of time and then unloaded. Initially, the material undergoes instantaneous elastic deformation, in a similar manner to that for an archwire alloy. However, as the load is maintained, there is a retarded elastic deformation (or anelastic deformation), followed by a viscous or creep deformation that is irreversible if the applied load is sufficiently great. Upon unloading, the instantaneous elastic strain is recovered immediately, followed by a decay of the retarded elastic strain until only the permanent strain remains. This behavior is frequently described in terms of the creep compliance,

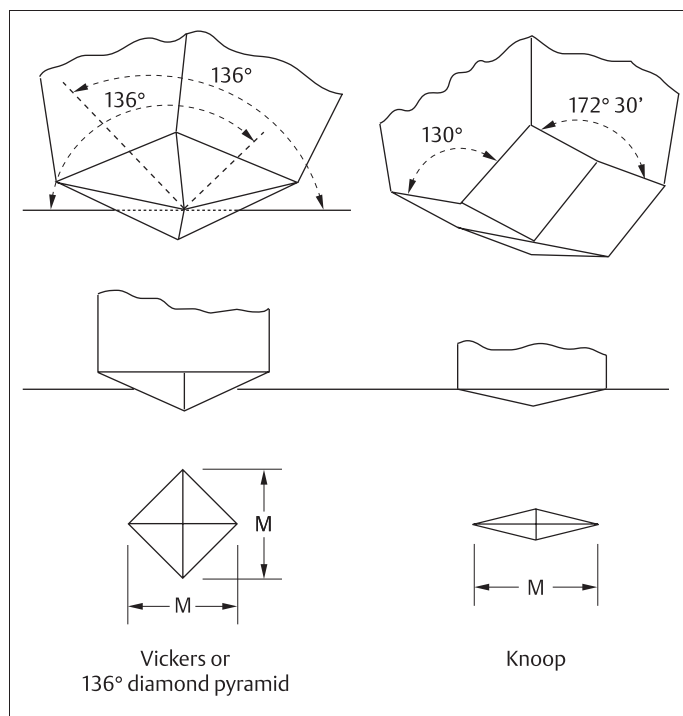


Fig. 1.12 Geometry of diamond indenters and schematic appearance of surface indentations for the Vickers and Knoop microhardness tests. The lengths of the diagonals designated by M are measured microscopically. (Adapted from Anusavice, 1996)

which is the quotient of the total strain in the viscoelastic material and the stress. The creep compliance thus contains the three contributions from the instantaneous elastic deformation, the retarded elastic deformation, and the permanent deformation.

Many investigators have employed models using springs and dashpots to describe the mechanical behavior of viscoelastic materials. These mechanical models employ various combinations of Maxwell and Voigt-Kelvin elements, consisting of a spring and a dashpot

in series and parallel, respectively. The spring is the basic linear elastic element, for which the force and displacement are linearly related through the spring constant by Hooke's law. This is analogous to the linear relationship between stress and strain through the modulus of elasticity below the elastic limit. The dashpot is the basic linear viscous element, for which the force is linearly related to the rate of extension of the dashpot piston by the viscosity. The analogy is a linear relationship between stress and strain rate with the coefficient of

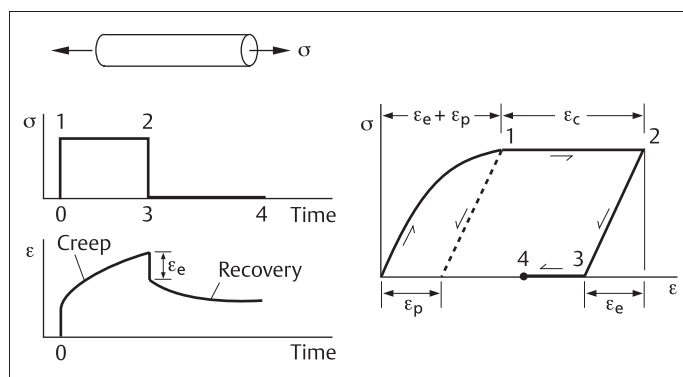


Fig. 1.13 Loading and unloading behavior for a viscoelastic material. The initial instantaneous elastic strain on loading corresponds to 1, and the region between 1 and 2 is a combination of the retarded elastic (anelastic) and the permanent (creep) strains. The first portion of the unloading curve between 2 and 3 is the recovery of the instantaneous elastic strain. The remaining permanent strain is designated by 4. (Adapted from Dowling, 1993)

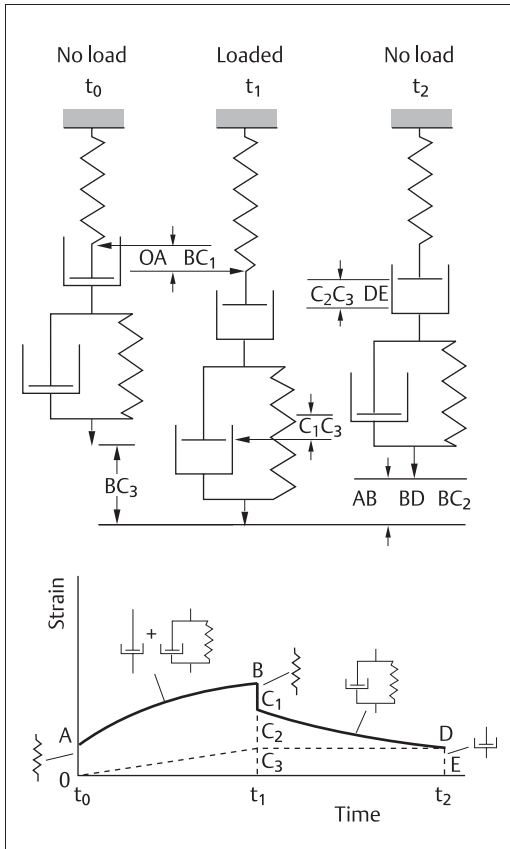


Fig. 1.14 Four-element model used to simulate the viscoelastic behavior of an elastomeric impression material. (Adapted from Craig RG, editor. Restorative dental materials, 9th ed. St. Louis: Mosby, 1993)

viscosity in shear as the constant of proportionality.

Figure 1.14 shows a four-element model that has been used to simulate the viscoelastic behavior of an elastomeric impression material subjected to the loading regime in Figure 1.13. Figure 1.15 shows a Maxwell-Weichert model that has been found to fit the force degradation behavior of orthodontic elastomeric modules, as discussed in Chapter 8. While a detailed discussion of the mathematical equations that describe the mechanical models in Figures 1.14 and 1.15 are beyond the scope of this textbook, the reader can readily visualize how the behavior of the elements in each model qualitatively leads to the observed viscoelastic behavior.

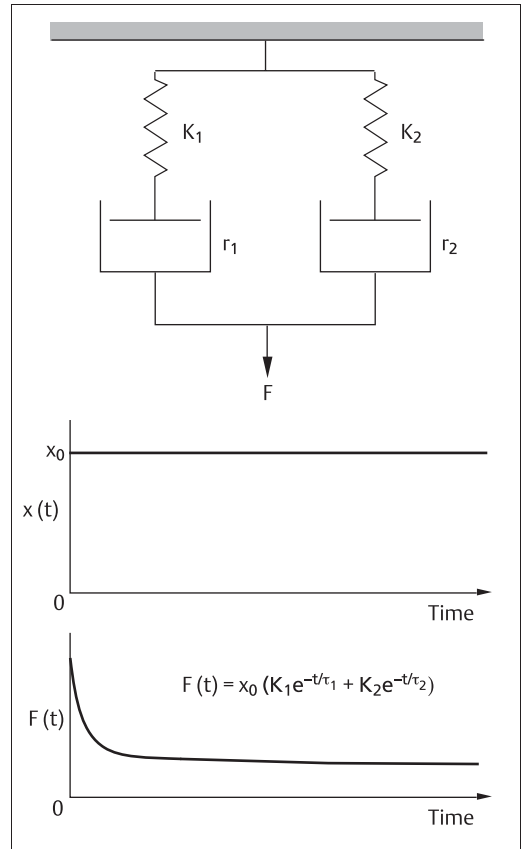


Fig. 1.15 Maxwell-Weichert model that has been used to simulate the force degradation behavior of orthodontic elastomeric modules. (From Stevenson and Kusy, 1994)

Surface Property Concepts for Orthodontic Materials

The interatomic bonding environment for atoms at the surface of a material, in either the solid or liquid state, is necessarily significantly different from that for atoms in the bulk material. The presence of unsatisfied or modified interatomic bonds for the surface atoms gives rise to a surface energy, traditionally reported in the cgs (centimeter-gram-second) system units of ergs/cm², rather than the SI units of J/m², where 1 J/m² = 10³ ergs/cm². This is the amount of energy required to create a unit surface area of the material. Alternatively, the surface tension may be con-

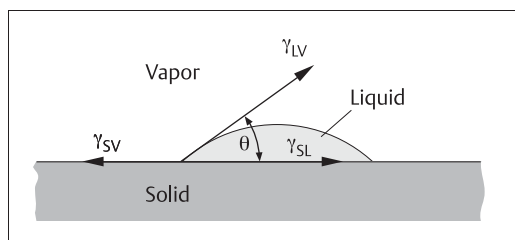


Fig. 1.16 Generalized concept of the three interfacial energies and the surface tension for a liquid droplet on a solid surface. (From Guy and Hren, 1974)

sidered, which is the amount of force required to extend the surface of a material by unit length. The surface tension has also been traditionally reported in the cgs units of dyn/cm, rather than in the SI units of N/m, where $1 \text{ N/m} = 10^3 \text{ dyn/cm}$. It can be seen that the basic units of surface energy (energy/area) and surface tension (force/distance) are the same.

Figure 1.16 illustrates a liquid droplet on a solid surface, where the three interfacial energies and the contact angle (θ) are designated. The interfacial energies exist between the solid and liquid (γ_{SL}), the liquid and vapor (generally air) (γ_{LV}), and the solid and vapor (γ_{SV}). Considering an equivalent force balance in the horizontal direction in Figure 1.16 for unit area and distance, the interfacial energies and contact angle are related by the expression

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} (\cos \theta)$$

Values of the contact angle have been used extensively in a wide range of dental materials science areas to report the wettability of various liquids to solid materials. Conventionally, good wetting corresponds to $\theta < 90^\circ$, whereas perfect wetting and complete absence of wetting (both never achieved in practice) would correspond to $\theta = 0^\circ$ and $\theta = 180^\circ$, respectively.

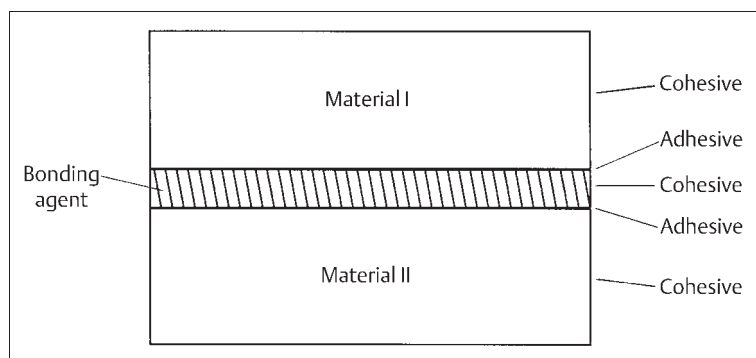
Surface properties are highly important for the bonding of orthodontic brackets to etched enamel, which is discussed in detail in Chapter 5. In order for the initially unpolymerized fluid bonding resin to penetrate into the capillary spaces of the etched enamel, the resin must wet the enamel. The rate of penetration into these capillary spaces depends upon the penetration coefficient (PC), which is given by

the expression $PC = \gamma (\cos \theta) / 2 \eta$, where the surface tension (γ) is equivalent to γ_{LV} and η is the viscosity of the fluid resin.

When bonding failures are observed, either visually or microscopically, in order to determine the failure modes, these failures are characterized as primarily adhesive or cohesive. Frequently, mixed-mode failure occurs, where there are both cohesive and adhesive failure sites. Cohesive failure refers to a failure through only a single material, where cohesive forces between the same atomic species are involved. Adhesive failure refers to failure at the interface between two different materials, where adhesive forces between two different atomic species are involved. The locations of cohesive and adhesive failure for two different materials that have been bonded to each other are illustrated in Figure 1.17. When assessing the failure modes in bonding systems, high-magnification observations with the scanning electron microscope are recommended, since examination with the optical microscope can be misleading because of the limit of less than $\times 500$ useful magnification and the limited depth of focus.

Recent research suggests that the surface properties of orthodontic bracket materials can have significant influence on early pellicle formation. A standard series of six liquids and measurements of contact angles were used to determine the critical surface tension, the total work of adhesion, and its components due to polar and nonpolar forces for raw materials utilized to fabricate metallic, ceramic, and polymeric brackets (Chapter 7). It was necessary to employ the raw materials because of differences in the geometries, surface compositions (including the presence of a hydrophobic silane coating on ceramic brackets) and surface roughness of commercial brackets. The highest critical surface tension was found for stainless steel (40.8 dyn/cm), followed by polycarbonate (32.8 dyn/cm) and alumina (29.0 dyn/cm), suggesting greater plaque-retaining potential with stainless steel brackets. A similar ranking among the three bracket materials was found for the total work of adhesion and its polar and nonpolar components. For the three materials, the nonpolar component of the work of adhesion was higher than the polar component, suggesting the likelihood of an increased proportion of microorganisms having dispersive

Fig. 1.17 Locations of simple cohesive (C) and adhesive (A) failure sites for two different materials that have been bonded to each other



van der Waals forces as the predominant attachment mechanism.

Variations observed by Fourier transform infrared spectroscopy (Chapter 3) in the adsorbed biofilms for two human subjects, following 30 and 60 minutes of intraoral exposure, suggested that there was an influence of the surface properties of these substrates on the structure of the pellicle formed *in vivo*. However, a subsequent *in vitro* study of the adherence of *Streptococcus mutans* to metal,

ceramic, and polymeric orthodontic brackets found that the initial affinity of this pathogen for metal brackets was significantly lower than that for ceramic and polymeric brackets. Moreover, a saliva coating caused decreased adherence to all three bracket materials. Additional complementary *in vitro* and *in vivo* studies will be needed to resolve this uncertainty about the microbial attachment to orthodontic brackets and its clinical relevance.

Structures of Orthodontic Materials

Metallic Materials

The alloys for archwires (Chapter 4) and brackets (Chapter 7) are used in the wrought form, where the shape is determined by the manufacturer using thermomechanical processing (mechanical deformation at elevated temperatures). The starting point is the formation of an ingot by melting the component metals together and allowing the alloy to solidify in a mold. After solidification, the alloys have a polycrystalline structure, consisting of microscopic single crystals (termed grains). These cast alloys are subjected to a series of mechanical deformation operations at elevated temperatures that result in a decrease in the cross section and severe deformation of the initial grain morphology for the cast microstructure. For example, the microstructure of a wire consists of highly elongated grains with a microscopic appearance analogous to that of parallel strands of spaghetti. An analogous distinctive appearance is found for the microstructure of

a metallic orthodontic bracket. In contrast, the microstructure of a dental gold alloy casting consists of equiaxed grains that have very similar dimensions. The alloy microstructures are determined by polishing the surfaces with a series of abrasives, ending in a submicrometer slurry (typically 0.05 μm) that does not leave visible scratches, followed by use of an appropriate etchant (either an immersion or electrolytic etching technique).

The alloys for orthodontic wires and brackets have relatively complex compositions and can consist of more than one structure (phase). While X-ray diffraction can be used to investigate the phase relationships in an orthodontic alloy (Chapter 3), there is difficulty detecting secondary phases present in small proportions with this technique, and examination of the polished and etched microstructures with the optical microscope and scanning electron microscope is recommended.

Phase diagrams are used to portray the phases present in alloys as a function of composition

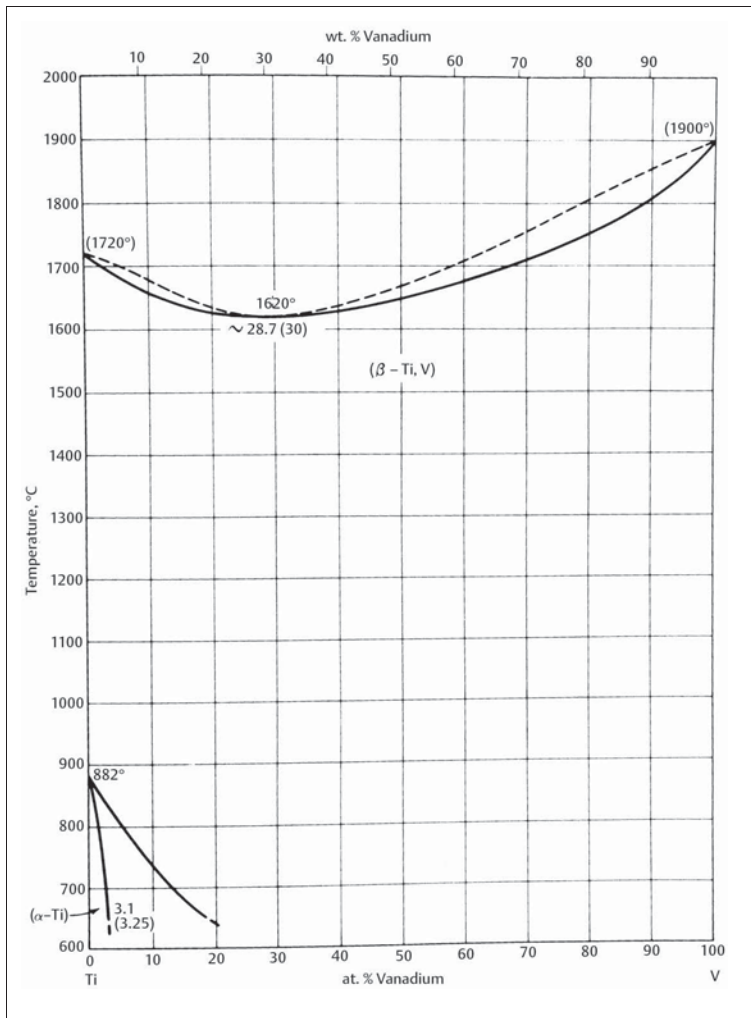


Fig. 1.18 Phase diagram for the Ti-V binary alloy system. (From Brick *et al*, 1977)

and temperature. A phase is a region having a specific composition and structure, and separated from other phases by a boundary. Phases can be in the solid or liquid state. The vapor phase, which is always present, is generally ignored in most materials science applications because of its very low concentration and minimal influence. Since these diagrams are obtained in the laboratory under conditions that approach equilibrium as much as possible, they are frequently referred to as equilibrium diagrams. Only those phase diagrams for simple binary alloys consisting of two component elements can be fully portrayed in two dimensions. The horizontal axis represents

composition, and the vertical axis represents temperature.

Figure 1.18 presents the phase diagram for the binary Ti-V system. At the left edge of this figure, it can be seen that pure titanium has the α (hcp) structure until 882°C, where it transforms to the β (bcc) structure; the melting temperature is 1720°C. At temperatures below about 1620°C, titanium and vanadium form a substitutional solid solution, in which vanadium atoms are located on the sites normally occupied by titanium atoms in its crystal structure. In the top portion of this diagram, the upper line, termed the liquidus, and the lower line, termed the solidus, define a two-phase

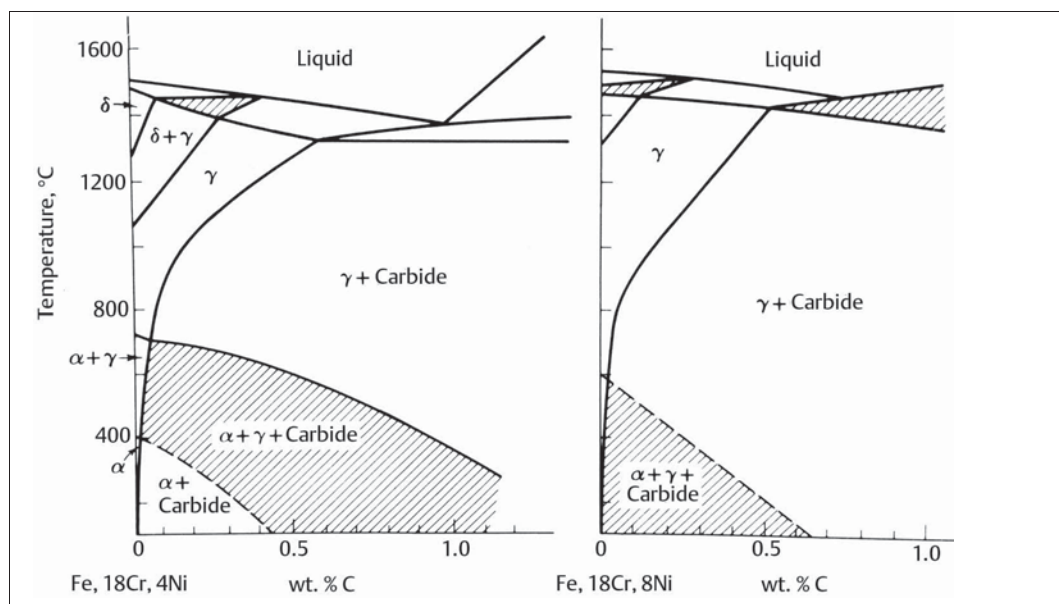


Fig. 1.19 Quasibinary phase diagrams for Fe-18Cr-4Ni and Fe-18Cr-8Ni (wt%) alloys as a function of carbon content. Up to at least 0.5% C, the carbide is $(\text{CrFe})_4\text{C}$. (From Brick *et al*, 1977.) These two diagrams show that increasing the percentage of nickel increases the temperature range for stability of the austenite (γ) phase.

region corresponding to coexisting solid and liquid phases as the alloy undergoes solidification. Above the liquidus curve, all alloy compositions are in the liquid state; below the solidus curve, all alloy compositions have completed solidification. In the lower left corner of the figure, the region of stability for single-phase α -structure alloys is indicated. The region between the two curves corresponds to a two-phase region of coexisting solid α and β phases. It can be seen that the presence of vanadium causes the β phase to exist at a lower temperature than would ordinarily occur for pure titanium. Hence, vanadium is a stabilizing element for the β phase of titanium.

Figure 1.19 presents a quasibinary phase diagram for Fe-18Cr-8Ni (wt%) alloys containing varying amounts of carbon up to 1.0%. This phase diagram is relevant to the discussion of austenitic stainless steel orthodontic wire alloys in Chapter 4. With four component elements in this case, a different strategy is needed for indicating alloy compositions. The origin at the left corner of the right phase diagram corresponds to the baseline composition of 74% Fe, 18% Cr, and 8% Ni. On the horizontal axis, the percentage of iron in the quaternary alloy de-

creases as the carbon content increases. Under equilibrium conditions the alloy structure is three-phase ($\alpha + \gamma + \text{carbide}$) or two-phase ($\gamma + \text{carbide}$) at room temperature, depending upon the carbon content, where the carbide phase has the composition $(\text{CrFe})_4\text{C}$. Alloy compositions having less than about 0.65% C contain both the α (ferritic) and γ (austenitic) phases, rather than the single-phase austenitic structure (along with the carbide phase).

Among the three classes of orthodontic materials, only metals have the capability of undergoing extensive permanent deformation at room temperature. This characteristic is often termed ductility although, strictly speaking, ductility in dental materials science traditionally refers to the ability of a metal to undergo extensive permanent tensile deformation before fracturing. This plastic deformation is accomplished by the generation and movement of vast numbers of defects termed dislocations in the atomic structure when the stress in the metal reaches the PL or YS.

A schematic illustration of an edge dislocation in a metal with a cubic structure is shown in Figure 1.20. The dislocation lies at the edge of the missing half-plane of atoms and moves

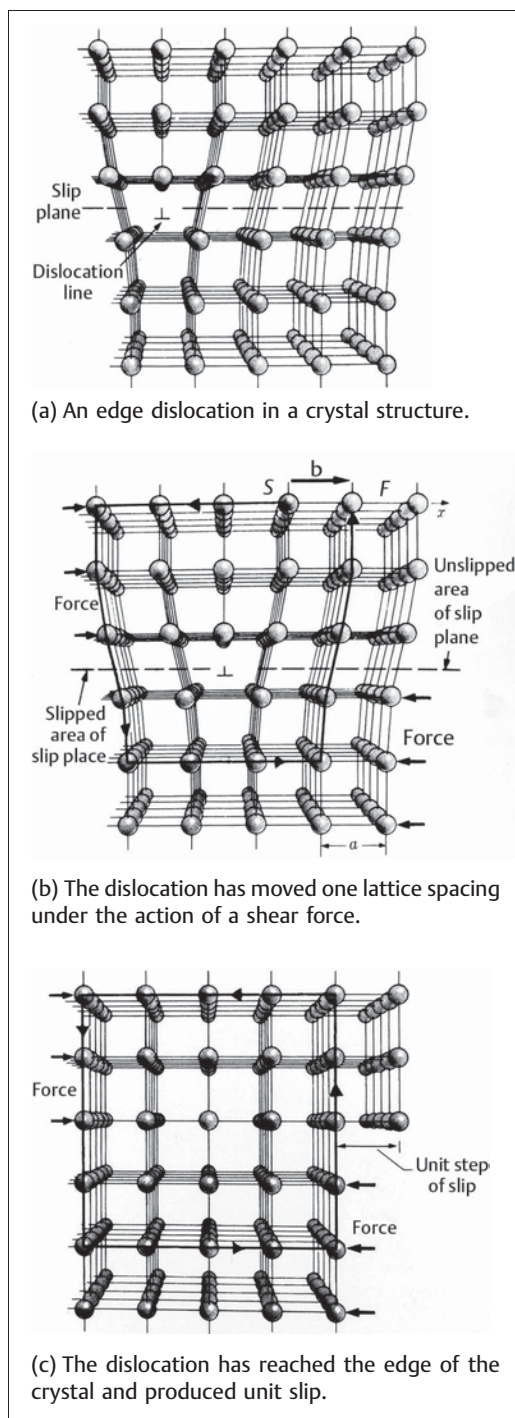


Fig. 1.20 Illustration of an edge dislocation in a metal with a cubic structure and its movement along a slip plane in response to a shear stress. (Adapted from Guy and Hren, 1974)

along a slip plane in response to a shear stress (or the shear stress component of a tensile or compressive stress). Movement of the dislocation causes the portion of the atomic structure on one side of the slip plane to be displaced (to undergo slip) with respect to the structure on the other side of the slip plane. The combination of this slip direction and the slip plane is referred to as a slip system. Since the dislocation movement in Figure 1.20 creates only one unit of slip deformation at the atomic level, it can be appreciated that practical levels of permanent deformation in metals require the generation and movement of vast numbers of dislocations. While the edge dislocation is the easiest configuration to visualize, other dislocation geometries also exist in actual metals. The study of dislocations requires the use of transmission electron microscopy, for which specimen preparation and interpretation of the observations are advanced subjects in materials science. Nevertheless, the reader can understand many important aspects of the mechanical properties of metals by considering the model suggested by Figure 1.20.

A second important mode of permanent deformation at the atomic level for the nickel-titanium orthodontic alloys is twinning. Figure 1.21 provides a schematic illustration of this process, where it can be seen that the atoms on either side of the twinning plane have a mirror orientation relationship with each other.

The fundamental mechanisms for strengthening of a ductile metal are generally associated with the different means by which dislocation motion is impeded, and increases in the strength of a metal are accompanied by increases in hardness and decreases in ductility. The major strengthening mechanisms for orthodontic alloys arise from the addition of alloying elements to the principal atomic species in the composition and the effect of extensive cold working (work hardening) during fabrication of the archwire or bracket.

In a single-phase alloy forming the usual substitutional solid solution, this disordered solid solution impedes dislocation motion more than would occur for the crystal structure of the pure solvent metal. Dislocation movement is more difficult in multiphase alloys containing two or more phases with different compositions and generally different crystal structures,

because the various phases often have different slip systems and dislocations cannot cross the boundaries between grains of the same phase or different phases. Precipitation hardening occurs when the addition of appropriate amounts of alloying elements creates precipitates in the solid solution formed by the solvent element; such precipitates also impede the movement of dislocations.

When a ductile metal is cold-worked, *i.e.*, experiences substantial permanent deformation at room temperature or elevated temperatures below the recrystallization temperature (to be discussed later), structural changes occur at different levels. For example, the many dislocations generated at the atomic (transmission electron microscopy) level impede the motion of individual dislocations, resulting in work hardening through a variety of dislocation interaction processes. As previously noted, the extensive mechanical deformation required for fabrication of an archwire or a bracket greatly changes the morphology of the grains in the microstructure at the optical and scanning electron microscopy levels. This wrought microstructure has increased interference to dislocation movement, resulting in higher yield strength.

Such extensive mechanical deformation causes considerable strain energy to be stored in the atomic structure of a metal, and the effects of cold working can be modified or eliminated by appropriate elevated-temperature heat treatment. Three annealing stages are pos-

sible, where annealing here refers to isothermal heat treatment for simplicity. The recovery stage, which occurs at the lowest temperatures, involves the annihilation of dislocations (by so-called glide and climb processes of movement that are beyond the scope of this book) without significant changes in the cold-worked structure visible with the optical or scanning electron microscope. A recovery heat treatment is often performed to eliminate residual stresses in appliances fabricated from stainless steel archwires and to minimize the likelihood of fracture, as discussed in Chapter 4. At higher heat treatment temperatures and longer times, recrystallization may occur, in which new stress-free equiaxed grains form and entirely consume the original cold-worked structure. If this heat treatment is continued for prolonged times, further grain growth of the recrystallized structure takes place. Recrystallization is to be avoided during the heat treatment of orthodontic wires because replacement of the wrought microstructure with an equiaxed grain structure yields substantially inferior mechanical properties. Figure 1.22 shows schematic microstructures of the grains in a bent archwire segment for the as-received cold-worked condition and after subsequent heat treatment where recrystallization and grain growth occurred. Recrystallization heat treatments are used by manufacturers during the fabrication of orthodontic wires, because the original cast ingot must be subjected to several stages of mechanical deformation and heat

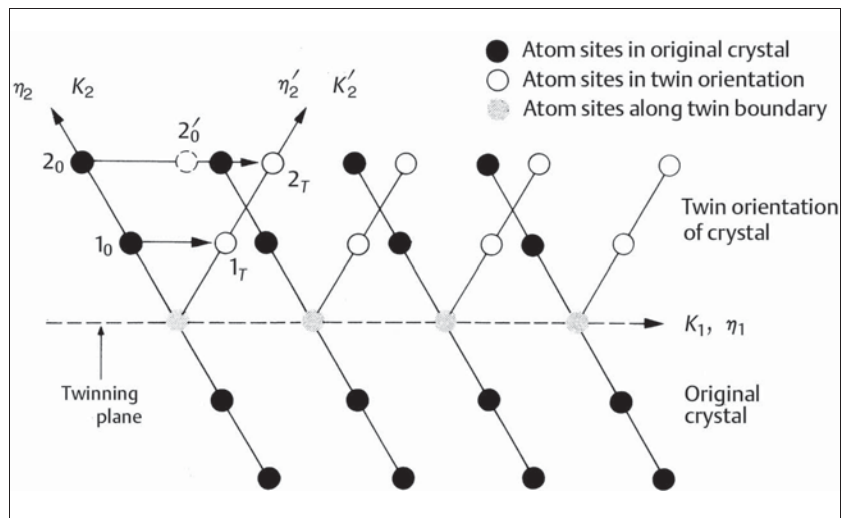


Fig. 1.21
Illustration of the atomic orientation relationships after twinning in a metal. (From Guy and Hren, 1974)

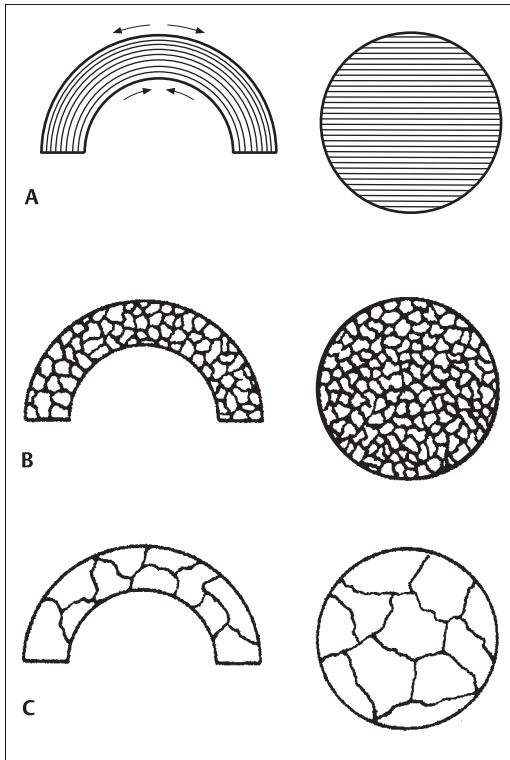


Fig. 1.22 Schematic appearance of grains in the microstructure of an archwire in the initially bent condition (A), and after recrystallization (B) and subsequent grain growth (C). The highly deformed grains in the as-received archwire and the cold-worked microstructure (A) appear as closely spaced lines parallel to the wire axis. This microstructure is not altered by a properly performed recovery heat treatment to relieve residual stresses. (Adapted from Craig, 1997)

treatment before the final cross-sectional dimensions are obtained.

A highly important consideration for orthodontic alloys is their *in vivo* corrosion performance, since the release of significant quantities of metallic ions might have adverse effects on the health of patients. The corrosion of dental and medical alloys is generally studied under *in vitro* conditions, using a potentiodynamic polarization technique in which the corrosion current from the alloy is measured over a range of electrical potentials. A three-electrode arrangement is employed. One electrode is prepared from the alloy under investigation; an inert counterelectrode is used to complete the electrochemical cell, and a reference elec-

trode (typically the standard calomel electrode) is also present. The corrosion medium is typically a saline solution, an artificial saliva, or some other simulated body fluid.

Potentiodynamic polarization plots for nickel-titanium orthodontic alloys are shown in Figure 1.23. The vertical axis is the potential difference between the alloy and the standard calomel electrode (SCE), and the horizontal axis is the current for the alloy specimen. The lower part of each plot, which is of minimal interest, is the cathodic component where reactions such as the reduction of water and the evolution of hydrogen are taking place. At the corrosion potential, the alloy becomes anodic and the corrosion current in the upper portion of the plot increases as the potential difference with respect to the reference electrode increases. Because the orthodontic alloys have thin surface oxide films that provide corrosion resistance *in vivo*, as discussed in Chapter 4, there is an extended region where the corrosion current changes little with increases in potential. Finally, the applied potential on the alloy reaches a sufficiently high value that the surface oxide film breaks down, and the corrosion current then increases rapidly with further increases in potential. Plots similar to Figure 1.23 can be used to compare the *in vitro* corrosion performance of different orthodontic alloys by considering the value of potential at which the passivating surface oxide film breaks down.

Ceramic Materials

Ceramic materials are used in orthodontics for brackets (alumina and zirconia) and as filler particles in cements. These applications will be discussed in Chapters 7 and 11. In addition, ceramic/polymer composite material wires have been proposed, as described in Chapter 4.

As previously discussed in this chapter, crystalline ceramic materials have a combination of covalent and ionic bonding, with minimal dislocation movement at room temperature. By definition, dislocations cannot exist in noncrystalline materials. Accordingly, the ceramic materials used in orthodontics are completely brittle, with the stress-strain plot being a straight line up to the point for fracture (Fig. 1.24), since there is no mechanism that

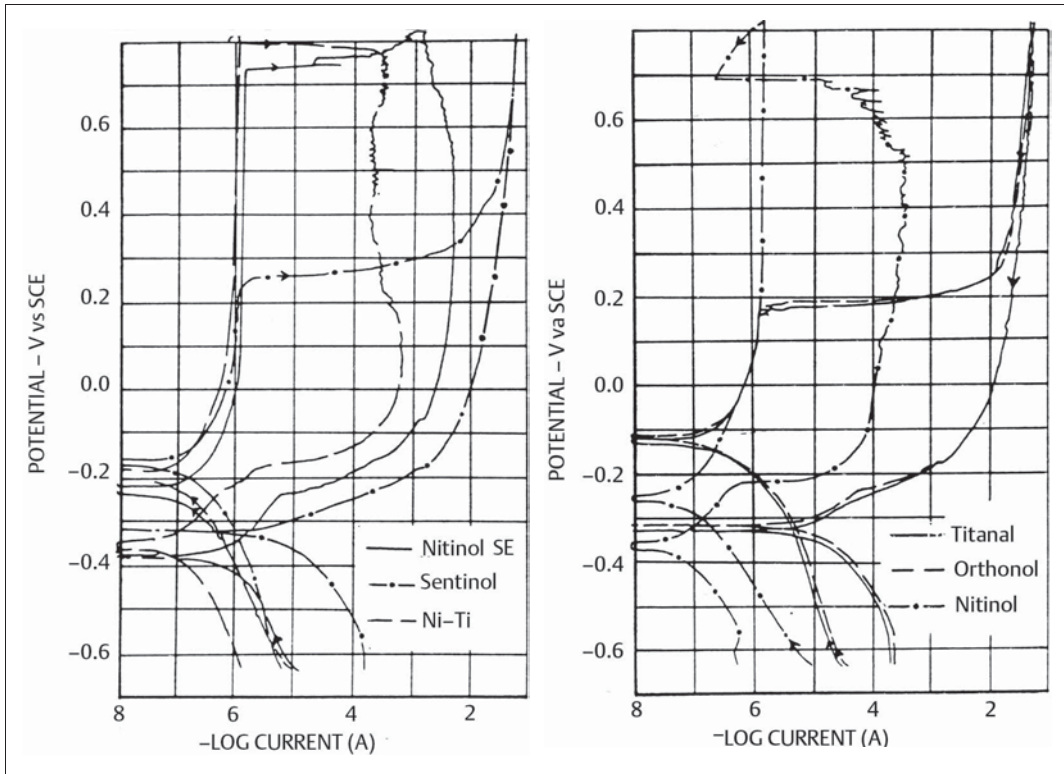


Fig. 1.23 Potentiodynamic polarization plots for nickel-titanium orthodontic wire alloys. (From Khier and Brantley, 1997)

permits permanent deformation under clinical conditions. However, the strong interatomic bonding accounts for the advantageous chemical inertness of dental ceramics, notably dental porcelain and the ceramic brackets.

The fracture behavior of these ceramics is controlled by the influence of flaws such as surface cracks and other microscopic defects or internal pores. When the ceramic is subjected to stress, in the vicinity of these so-called Griffith flaws the nominal stress becomes greatly magnified, and fracture occurs by crack propagation when the local stress exceeds the cohesive strength of the material. For example, it can be shown that the maximum stress in the vicinity of a round pore is three times the nominal stress. The local stress near the tip of a crack is proportional to $(l/\rho)^{1/2}$, where l is the crack length and ρ is the radius of curvature at the crack tip, so that sharp cracks are effective sources of stress concentration. Elimination of surface imperfections and internal porosity is

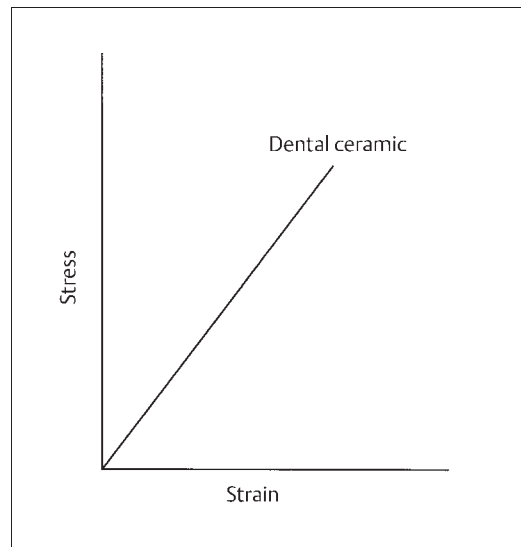


Fig. 1.24 Schematic stress-strain curve for a dental ceramic that undergoes no permanent deformation before fracture

particularly important for achieving the highest levels of mechanical properties for the ceramic brackets. These and other brittle materials are much stronger for compressive loading, which tends to close cracks, than for tensile loading, which tends to open cracks and facilitate crack propagation.

There will be a population of flaws for a test sample of nominally identical ceramic specimens, resulting in substantial scatter when mechanical properties are measured experimentally. The most appropriate method for analysis of the failure of brittle materials (including the resins discussed in the next section) is use of the Weibull statistical distribution, which is based upon the weakest-link concept. The plot of $\ln \{ \ln [1/(1 - P)] \}$ vs. $\ln x$, where P is the cumulative failure probability at a given value of the measured variable x (such as strength), yields a straight line (Fig. 1.25). The slope of this line, termed the Weibull modulus, is greater for smaller scatter in the measured variable. Additional information on the applications of Weibull statistics to dental materials is given in the references at the end of this chapter.

When the most popular ceramic bracket materials are considered, polycrystalline alumina has considerably better fracture resistance than single-crystal or monocrystalline alumina (sapphire). The path of crack pro-

pagation in polycrystalline alumina is irregular, generally occurring along grain boundaries, but complex transgranular patterns can also arise (Chapter 7). In contrast, while the stress to initiate failure is greater for the single-crystal alumina brackets, crack propagation occurs easily owing to the lack of obstacles in the microstructure.

An important characteristic of the brittle ceramics is fracture toughness, which is considered to be a fundamental material property when measured under plane-strain conditions (Chapter 2). The fracture toughness provides a measure of the force or energy required for crack propagation, and the fracture toughness under mode I tensile crack-opening conditions (K_{IC}) (The subscript is pronounced "one-see.") is generally determined. One popular experimental technique involves the fracture of notched specimens in three-point bending, where a formula relates K_{IC} to the force for failure and the specimen dimensions. As discussed in Chapter 2, it is essential that the specimen dimensions, particularly the breadth, be controlled to maintain the two-dimensional state of plane strain. Another experimental technique, which is highly suitable for small specimens such as ceramic brackets, involves use of the Vickers hardness testing machine to place microscopic indentations on the surface of the ceramic being evaluated. Cracks form

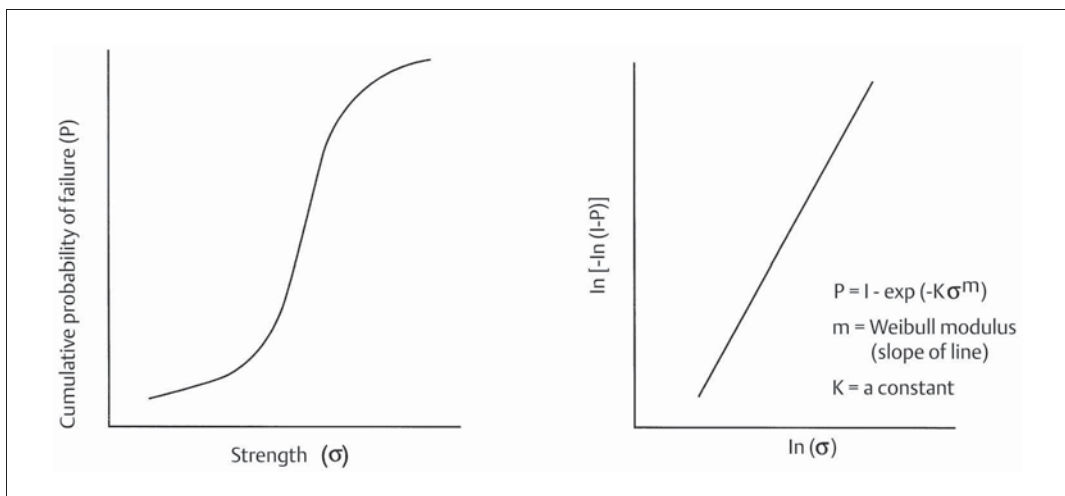


Fig. 1.25 Plot used for the Weibull analysis of experimental strength data (e.g., bond strength between brackets and enamel). The raw data must first be ranked in numerical order to determine the cumulative failure probability

at the tips of the indentation (Fig. 1.26), and there is a relationship between K_{Ic} and the indenting load. However, Knoop indentations must also be placed on the surface to obtain the ratio of elastic modulus and hardness for use in this relationship, unless the former is known for the particular ceramic.

As discussed in Chapter 7, there has been interest in zirconia brackets because of the possibility of obtaining higher fracture toughness than that available with polycrystalline alumina brackets. Pure zirconia undergoes a phase transformation from the tetragonal structure to the monoclinic structure when cooled through the 1100–1200 °C range, with a volume change of approximately 3% that can cause fracture of the ceramic. Small additions of yttrium oxide (Y_2O_3) and hot isostatic pressing can be employed to achieve very small grain sizes of yttrium-oxide-partially-stabilized zirconia (YPSZ) ceramics having a metastable tetragonal structure. Transformation toughening, with resulting high values of fracture

toughness ($9 - 10 \text{ MPa} \cdot \text{m}^{1/2}$), is observed for YPSZ ceramics, in contrast to the fracture toughness values of 3.60 and $5.22 \text{ MPa} \cdot \text{m}^{1/2}$ that have been reported for two brands of polycrystalline alumina brackets. Stress fields near the tips of propagating cracks cause a strain energy-absorbing martensitic transformation, and the resulting monoclinic grains hinder further crack propagation. However, as discussed in Chapter 7, difficulties in processing the zirconia brackets yield much lower mean fracture toughness values of $3.92 \text{ MPa} \cdot \text{m}^{1/2}$, compared to that for the YPSZ structure.

Polymeric Materials

As previously noted, a wide variety of polymeric materials are used in orthodontics: polyurethane elastomers for tooth movement, adhesive resins for bonding brackets to tooth structure, polycarbonate brackets (albeit with metallic slot inserts), impression materials, and new composite-material wires. These different materials are discussed in Chapters 4, 5, 7–10 and 12. The polymer matrix is of central importance for the glass-ionomer, zinc polycarboxylate, and resin cements, which are discussed in Chapter 11.

The elastomeric impression materials and polyurethane modules exhibit rubber elasticity. The unusual stress-strain diagram for this type of material is shown in Figure 1.27, where the plot of the initial region of elastic deformation has curvature rather than being a straight line as for metals and ceramics. The elastic limit occurs at the point of inflection where the curvature of the plot changes from concave-down to concave-up. The region of elastic deformation corresponds to reversible changes for the molecules in the polymeric structure. The absence of a linear region for Hookean elasticity in the stress-strain curve for an elastomer occurs because of the varying chain lengths and structures, whereas permanent deformation occurs from irreversible displacements between the polymeric chains, including rupturing of cross-links.

In contrast to metals and ceramics, whose mechanical properties are not greatly affected by changes in normal laboratory loading rates, the force delivery and relaxation behavior of the polyurethane elastomeric modules are

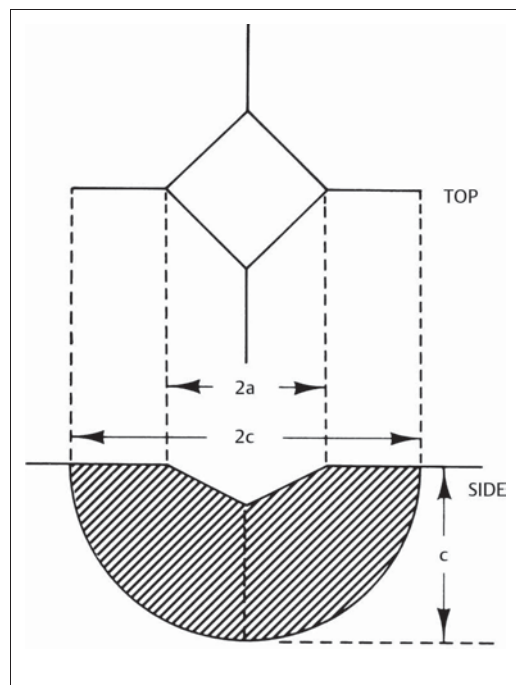


Fig. 1.26 Schematic appearance of a Vickers hardness indentation in a ceramic and the associated cracks at the tip of the indentation, used for obtaining the fracture toughness of a ceramic specimen. (From Morena *et al*, 1986)

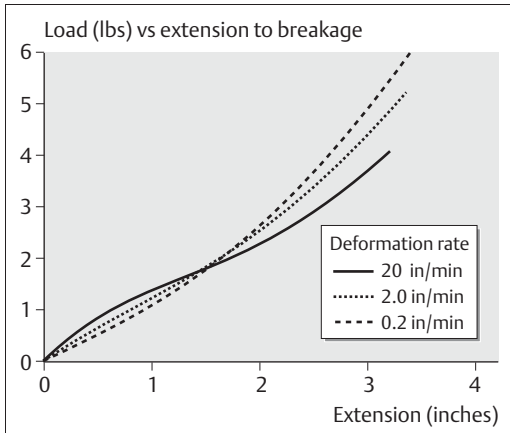


Fig. 1.27 Stress-strain curve for a polymeric material that exhibits rubber elasticity. (Adapted from Kovatch *et al*, 1976)

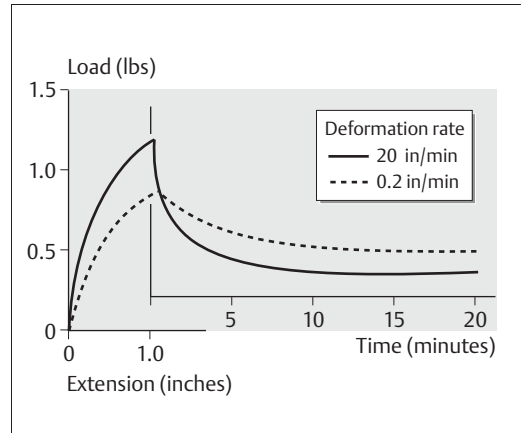


Fig. 1.28 Dependence of the force delivery and force relaxation on the rate of extension for a polyurethane elastomeric module used for tooth movement. (From Kovatch *et al*, 1976)

considerably affected by the rate of loading, as shown in Figure 1.28. It is recommended that clinicians activate the modules slowly *in vivo* to obtain the lowest rate of force degradation. Another example of the clinical importance of time-dependent mechanical properties of elastomeric materials is the clinical removal of a set

alginate impression, which should be done rapidly to minimize the time during which the material may undergo permanent compressive strain when being withdrawn past tooth undercuts. The tear strength and compressive strength are also greater for more rapid rates of loading.

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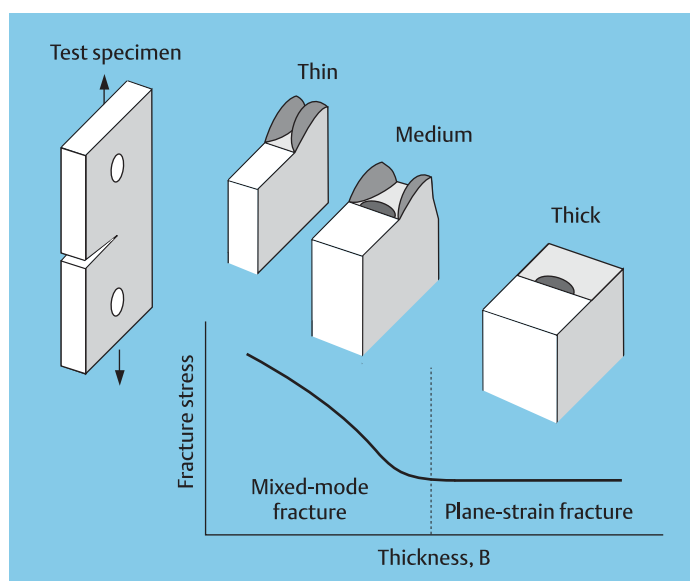
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2 Mechanics and Mechanical Testing of Orthodontic Materials

William A. Brantley

Theodore Eliades

Alan S. Litsky



Appearance of the fracture surface for a notched tensile test specimen as the fracture mode changes from a mixture of plane stress and plane strain to purely plane strain conditions

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of Mechanical Properties of
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Introduction

Basic knowledge of solid mechanics is important for an appreciation of biomechanical principles used in tooth movement and for understanding the important bending and torsion tests used to measure the mechanical properties of clinical relevance for orthodontic wires. Mechanical testing is employed in the biomaterials laboratory to evaluate the important properties of metallic, ceramic, and polymeric orthodontic materials that were discussed in Chapter 1.

In this chapter the major concepts for bending and torsional deformation of solids, and the origin of mathematical relationships that have been used to evaluate the mechanical

properties of archwires, will be presented. The two types of universal mechanical testing machines will be described, followed by consideration of experimental procedures for laboratory measurement of some mechanical properties of orthodontic materials. Particular emphasis will be placed upon bending tests, the evaluation of adhesive bond strength, and the measurement of fracture toughness. The diametral compression test and the measurement of fatigue behavior will also be discussed. Extensive information about other mechanical property measurements for dental materials is available in the Craig textbook.

Bending Deformation

Figure 2.1 shows a segment of a uniform rectangular beam subjected to pure elastic bending, *i.e.*, acted upon only by a bending moment that is of insufficient magnitude to cause permanent deformation. The beam may be considered to represent an orthodontic archwire. In order to have static mechanical equilibrium, the ends of this segment are acted upon by equal and opposite bending moments. From examination of Figure 2.1 it is apparent that, at the

top and bottom outermost surfaces, the length of the beam has experienced an increase (tensile strain) and a decrease (compressive strain) parallel to the axis, respectively. For a symmetric beam (round, rectangular, or square cross section), the material at the midplane does not experience any deformation. The undeformed midplane of the elastically bent beam is termed the neutral surface, and the trace of the neutral surface on the cross section

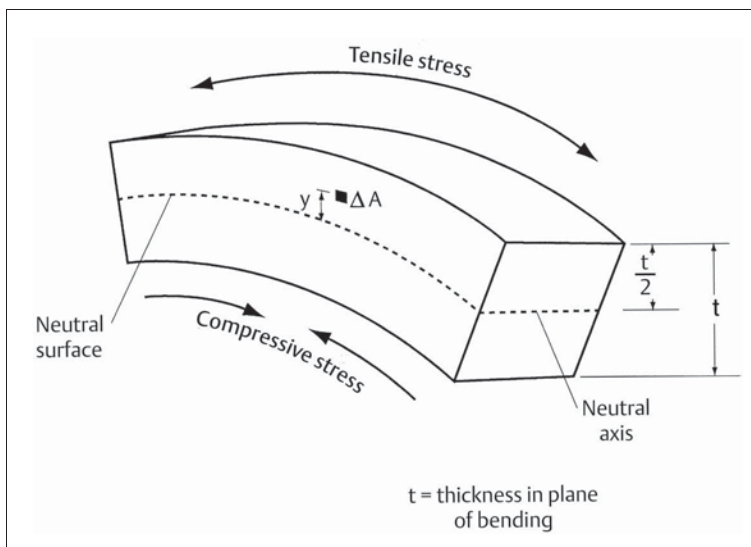


Fig. 2.1 A portion of a symmetric rectangular beam subjected to pure elastic bending. The location of the neutral surface is indicated, along with the position of the neutral axis on an axial cross section of the beam. An element of area (ΔA) located a distance (y) from the neutral surface is also shown

perpendicular to the beam axis is termed the neutral axis. Both the neutral surface and neutral axis are indicated in Figure 2.1.

Figure 2.2 shows that the stress in the beam varies linearly with distance from the mid-plane, reaching maximum values at the outermost surface. The corresponding strain is obtained by dividing the stress by the modulus of elasticity (Young's modulus) of the beam material, which has the same value for tensile and compressive stress. In textbooks on solid mechanics, force and moment balances are performed on a section of the beam (free-body diagram) to derive the elastic flexure formula. It is also assumed that plane surfaces perpendicular to the undeformed beam axis remain planar after the elastic deformation. The relationship between the stress (σ) developed in the beam as a function of the bending moment (M) and distance from the neutral axis (y) is

$$\sigma = \frac{My}{I}$$

where I represents the moment of inertia of the cross section. The moment of inertia is a geometric quantity that corresponds to the resistance of a particular cross section to bending and is given by the relationship:

$$I = \sum_i y_i^2 (\Delta A_i)$$

where the y_i are the distances of the elemental areas (ΔA_i) from the neutral axis and the summation is over all the elemental areas comprising the cross section of the beam. The contributions to the moment of inertia are greatest for the elemental areas farthest from the neutral axis, since each area is multiplied by the square of its distance from this centerline of the cross section (for a symmetric beam). This principle is exploited with the rectangular I-beam used in the construction of buildings, where the maximum amount of material is located farthest from the center (neutral axis) of the beam.

Since the largest value of y corresponds to the greatest distance (c) from the neutral axis to the surface of the beam, the maximum stress developed by the bending moment is given by

$$\sigma_{\max} = \frac{Mc}{I}$$

The section modulus (Z) is often defined as

$$Z = \frac{I}{c}$$

so that the maximum stress in the beam can be written alternatively as

$$\sigma_{\max} = \frac{M}{Z}$$

This expression is convenient to use when comparing the maximum stress developed in a series of orthodontic wires of varying cross-sectional dimensions. The relationship is analogous to the equation that defines normal stress (tensile or compressive) as the quotient of force and cross-sectional area. For bending, the role of force is assumed by the moment, and the section modulus provides information about the cross-sectional geometry of the beam.

Writing an integral expression for the moment of inertia as the elemental areas become infinitesimally small, it can be shown that for a round beam of diameter (d):

$$I = \frac{\pi d^4}{64}$$

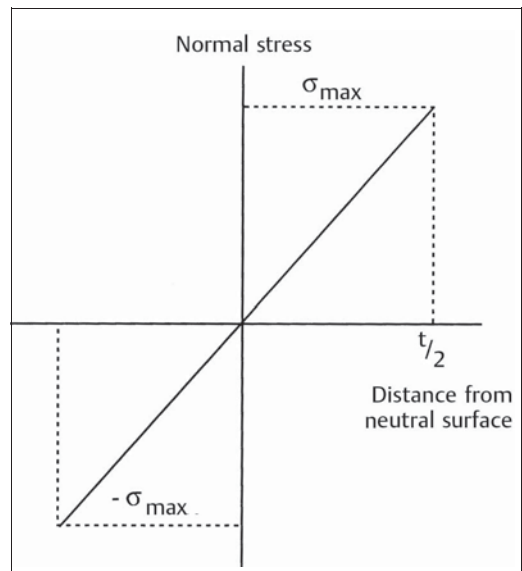


Fig. 2.2 Variation of the compressive and tensile stress with distance from the midplane of the bent symmetric beam in Figure 2.1

Table 2.1 Values of moment of inertia in bending for several orthodontic archwire sizes

Dimensions (inch)	Dimensions (mm)	Moment of inertia (I) (10^{-4} mm^4)
0.012 ^a	0.305	4.25
0.016 ^a	0.406	13.3
0.020 ^a	0.508	32.7
0.040 ^a	1.016	523
0.016 × 0.016 ^b	0.406 × 0.406	22.6
0.018 × 0.025 ^b	0.457 × 0.635	50.5 ^c
		97.5 ^d

^a Diameter of round wire.

^b Cross-sectional dimensions of rectangular wire.

^c Bent flatwise.

^d Bent edgewise.

For a rectangular beam of width w and thickness t in the direction of bending, the moment of inertia is given by

$$I = \frac{wt^3}{12}$$

Because of the dependence of I on the fourth power of diameter and the cube of thickness, there can be considerable differences in the resistance to bending of orthodontic archwires having different cross-sectional dimensions.

For comparison, the values of moment of inertia for several archwire sizes are listed in Table 2.1. The enormous differences in I are evident for the four round wires shown. The greater value of I for a square wire, compared to a round wire of the same cross-sectional dimensions, can be seen from the examples of the 0.406 mm diameter round wire and the 0.406 mm × 0.406 mm square wire. The bending direction has a substantial effect on the value of I for a rectangular wire, as shown

for the 0.457 mm × 0.635 mm wire bent in the edgewise ($t = 0.635$ mm) and flatwise ($t = 0.457$ mm) directions.

For a given value of moment or load, it can be shown that the elastic bending deflection of a beam (or archwire segment) is inversely proportional to its length. Consequently, the stiffness in bending for an archwire segment of length l is given by the following proportionality

$$\text{Stiffness} \propto \frac{EI}{l}$$

where the elastic modulus E represents the alloy contribution and I/l represents the segment geometry (cross section and length) contribution to stiffness. This relationship is useful for comparing the relative values of stiffness in bending for round and rectangular archwires of different alloys, using the preceding expressions for I and values of E given in Chapter 4.

Torsional Deformation

Figure 2.3 shows the stress distribution over the cross section of a circular beam (round orthodontic wire) of radius c subjected to torsional loading in the elastic range. It can be seen that the beam experiences shear stress, which varies linearly from zero at the center to

a maximum value ($\tau_{\max}$) at the surface. With the assumption that plane sections perpendicular to the beam axis remain plane after application of the torque (i.e., no warping of these planes occurs), a balance of the torque developed on all of the elemental areas (ΔA_i) of the cross sec-

tion and the external torque (T) yields the relationship

$$\tau_{\max} = \frac{Tc}{J}$$

where J is the polar moment of inertia, which is given by

$$J = \sum_i (\rho_i)^2 (\Delta A_i)$$

The ρ_i are the radial distances of the ΔA_i from the center. In the limit, as the elemental areas become infinitesimally small, the polar moment of inertia for a round beam is

$$J = \frac{\pi c^4}{2} = \frac{\pi d^4}{32}$$

For a round beam, the value of J for torsional loading is thus twice the value of I for bending. Accordingly, the values of J for the four round archwires in Table 2.1 are obtained by doubling the indicated values of I .

Expressions for the section modulus ($Z_T = J/c$) and maximum shear stress in torsion ($\tau_{\max} = T/Z_T$) for round beams can be written that are analogous to those previously shown for bending deformation.

The solid mechanics analysis for torsion of rectangular beams is mathematically complex because planar sections perpendicular to the beam axis become warped, as shown in Figure 2.4. The shear stress distribution in the twisted rectangular beam is illustrated in Figure 2.5, where it can be seen that the shear stress is zero at the corners and maximum at the midpoints of the long sides. The

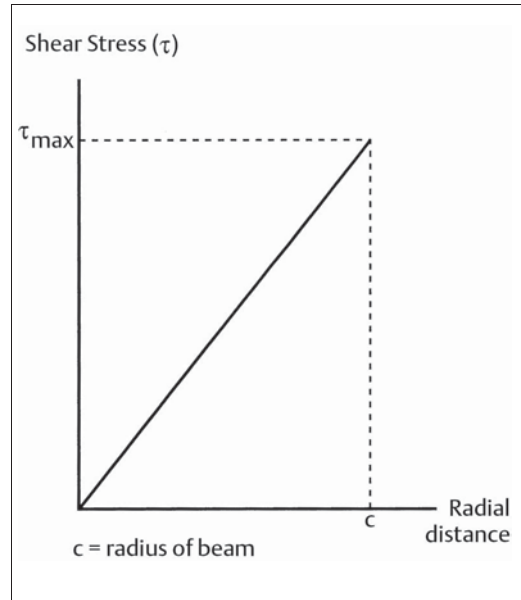


Fig. 2.3 Variation in elastic stress for a circular beam subjected to torsional loading

Table 2.2 Values of the parameter α used to calculate the maximum shear stress in rectangular beams subjected to torsion, as a function of the ratio b/c (the longer and shorter dimensions of the cross-section, respectively). (From Popov, 1968)

α	b/c
0.208	1.00
0.231	1.50
0.246	2.00

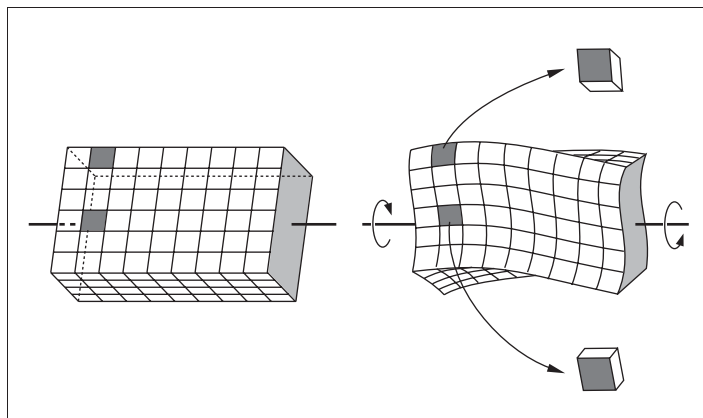


Fig. 2.4 Warping of a rectangular beam due to torsion. (From Popov, 1968)

maximum shear stress developed in a rectangular beam subjected to a torque T can be written as:

$$\tau_{\max} = \frac{T}{\alpha bc^2}$$

where b and c are the long and short dimensions, respectively, of the cross section and α is a parameter that depends upon the ratio (b/c). Values of α for three different (b/c) ratios that are useful for archwire and bracket base dimensions are given in Table 2.2.

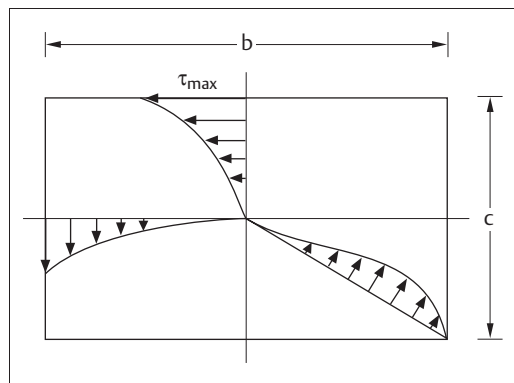


Fig. 2.5 Shear stress distribution in a rectangular beam subjected to torsion. (From Popov, 1968)

Mechanical Testing Methods for Orthodontic Materials

Mechanical Testing Machines and Experimental Procedures

Two types of sophisticated mechanical testing machines are used in the dental materials research laboratory. These machines are classified as screw-driven or servohydraulic, depending upon the method employed to move the crosshead and apply loads to the test specimen. A load cell senses the amount of force, and the raw data (the testing machine output) are typically plotted as load on the vertical axis and time or distance of crosshead movement on the horizontal axis. In order to plot stress-strain diagrams (Chapter 1), the values of load and change in specimen length must be converted to stress and strain, respectively. With the newer computer-controlled machines, the original specimen cross-sectional area and gauge length can be programmed, so that a direct plot of stress and strain is obtained.

The screw-driven machines (originally developed by Instron Corporation, Canton, MA, USA) have a large screw located at each end of the crosshead, whereas the servohydraulic machines (originally developed by MTS Systems Corporation, St. Paul, MN, USA) use the pressure of oil pumped into a hydraulic piston to move the crosshead. Because these mechanical testing machines can be employed for tension, compression, bending, or torsion tests, depending upon the specimen fixtures pur-

chased or designed by the experimenter, they have frequently been called universal testing machines in the research literature. Either type of machine will yield accurate values of the mechanical properties of orthodontic materials under the usual laboratory conditions of a single testing cycle. The servohydraulic machines are necessary for cyclic fatigue tests (discussed later in this chapter) performed at other than very slow rates.

Both types of mechanical testing machines are often referred to as constant strain-rate machines, because the rate of movement of the crosshead can be accurately set to designated displacement speeds (typically in units of mm/sec). If the gauge length of a specimen (Chapter 1) is expressed in the usual units of millimeters, then the strain rate may be considered to have the units of (mm/mm)/sec, or equivalently units of sec^{-1} . The standard tension or compression tests in materials science are performed at strain rates ranging from about 10^{-5} to 10^{-1} sec^{-1} . Typical crosshead speeds for mechanical testing of orthodontic materials vary from about 0.1 to 1 mm/min. As an example, for a specimen with a 10 mm gauge length that is tested in tension at a crosshead speed of 0.5 mm/min, the strain rate is $8.3 \times 10^{-4} \text{ sec}^{-1}$ or approximately 10^{-3} sec^{-1} . Servohydraulic machines can also be operated in the force control mode, where a set loading pattern is applied to the test specimen.

To determine accurate values of the elastic modulus in tension for archwires, which have high elastic moduli (stiffness) (Chapter 4), it is necessary to measure the length change of the specimen directly. An extensometer may be attached to the wire specimen, or some alternative method (such as an optical sensor) may be used. Accurate results will not be obtained if the crosshead movement (which can be read from the machine output) is used to calculate the specimen strain unless the data are corrected for the stiffness of the testing machine. Additional inaccuracy with the use of crosshead movement to determine strain can arise from slippage of archwire specimens at the grips used with the mechanical testing machine. For polymeric materials of low elastic modulus, the crosshead movement corresponds accurately to the specimen length change during tensile or compressive loading.

As previously noted in Chapter 1, the mechanical properties of metallic and ceramic dental materials are not greatly affected by loading rates normally used (*i.e.*, the rate of crosshead movement or strain rate), although variations in loading rate can have substantial effects on the mechanical properties of polymeric materials. Other than the nickel-titanium archwire alloys discussed in Chapter 4, there is minimal difference between the mechanical properties of metallic and ceramic dental materials determined at room temperature and 37°C. The mechanical properties of polymeric dental materials can have strong dependence upon temperature, which should be carefully investigated before extrapolating the results of room temperature measurements to clinical behavior at 37°C.

A highly convenient and inexpensive method for obtaining an approximately 37°C testing environment is to place a cardboard chamber around the specimen fixture area on the mechanical testing machine and use the radiant energy from a suitably positioned light bulb to provide the heating. The specimen temperature can be controlled to within about 1°C with this technique and monitored with a thermometer or thermistor. A wide array of more sophisticated environmental chambers are commercially available, and such chambers can also be fabricated inexpensively by the investigator.

Specific Tests for Evaluation of Mechanical Properties of Orthodontic Materials

Bending Tests

Bending tests have been popular for evaluation of the mechanical properties of archwires because of the relevance of bending deformation to the activation received by the archwires under clinical conditions. Three types of bending tests have been performed: a cantilever bending test using the Olsen stiffness tester, as recommended in the original form of American Dental Association (ADA) Specification No. 32, and three-point and four-point bending tests. The ADA standard is currently being revised, and it is expected that future methodology will employ the three-point bending test. The nature of the specimen loading for a cantilever beam and the three-point and four-point bending tests is shown in Figure 2.6. The cantilever bending test performed with the Olsen stiffness tester is somewhat more complicated than the example shown in Figure 2.6 because the fixed end of the specimen rotates while the other end of the test span is deflected by a bending plate.

While the three-point bending test is relatively simple to perform in the laboratory, this test has the disadvantage that there is a linear variation of the bending moment from a maximum at the loading point to zero at the two supports, as illustrated in Figure 2.7. This loading pattern can predetermine the failure location in a specimen. In contrast, Figure 2.7 shows that there is a uniform bending moment between the two inner loading points for the four-point bending test. In this case the specimen is allowed to fail at its weakest point, which is a highly useful feature when mechanical testing is being performed to identify structural weaknesses.

Brantley has derived a formula for modulus of elasticity (E) in bending obtained with the Olsen stiffness tester for 25 mm test spans of large-diameter (d) stainless steel and cobalt-chromium-nickel archwires that yields excellent agreement with values of E obtained in tension:

$$E = \frac{l}{2I} \frac{M}{\theta}$$

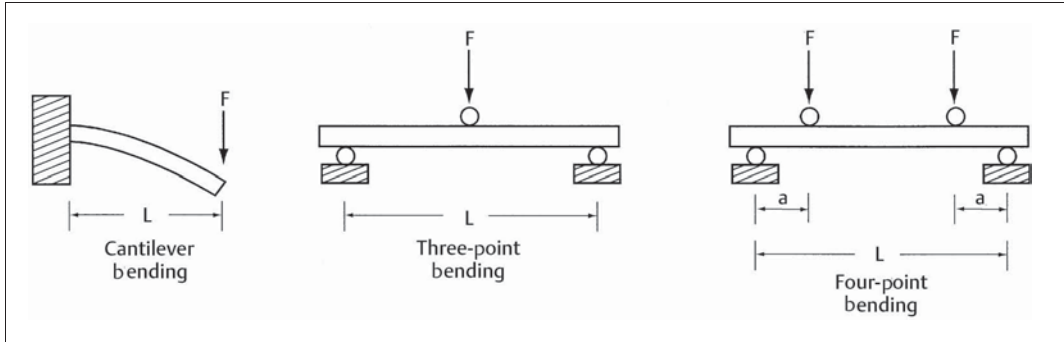


Fig. 2.6 Comparison of the specimen loading for a cantilever beam and the three-point and four-point bending tests

where l is the test span length, I is the moment of inertia, and M/θ is the slope of the bending moment-angular deflection plot. To use this formula, θ must be converted to radians (Chapter 1), and the ratio of l/d should be at least 15. However, this equation yields calculated values of E for 12.5 mm and 50 mm test spans that differ from the value for a 25 mm test span of the same wire, indicating a problem with the pure bending model used for the Olsen stiffness tester, since the true value of E would be independent of test span length.

The origin of this problem is the application of standard beam equations from solid me-

chanics to the elastic bending of orthodontic archwires that experience large deflections. Yoshikawa *et al* have shown that, for a cantilever beam specimen, it is necessary to resolve the applied force into two components that act perpendicular and parallel, respectively, to the wire axis. Only the former component causes the bending deflection, and the ratio of the two components changes with the amount of deflection.

For three-point and four-point loading of cantilever beams, the modulus of elasticity in bending can be calculated from the force-deflection plot, using equations from solid

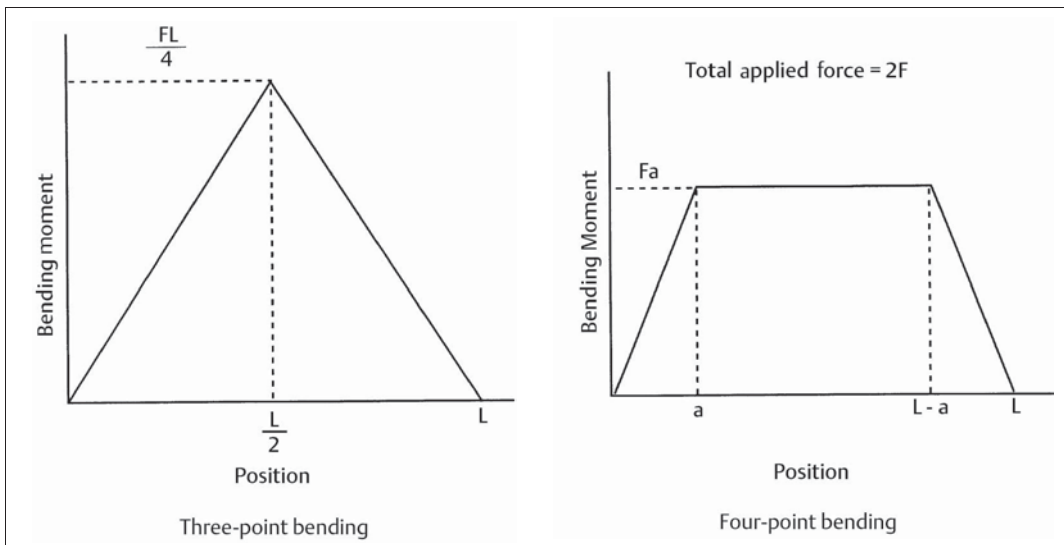


Fig. 2.7 Comparison of the variation in bending moment along the test span for specimens subjected to three-point and four-point bending

mechanics. For three-point bending, the maximum deflection (y) of the beam is given by

$$y = \frac{FL^3}{48EI}$$

where F is the applied force and L (Fig. 2.6) is the test span length. For four-point bending, the maximum deflection is determined from

$$y = \frac{Fa}{24EI} (3L^2 - 4a^2)$$

where a is the distance between an inner loading point and the adjacent outer support (Fig. 2.6), F is the applied force at each inner loading point (total applied force of $2F$), and the other symbols have the same meanings as before. The expression for four-point bending becomes the same as that for three-point bending if a is set equal to $(L/2)$ and the total force on the specimen is the same for each loading mode. Using relationships derived for the elastic bending deflection of triple-stranded archwires, Kusy and his colleagues have determined reasonable values of the elastic modulus for the wire alloys from three-point and four-point bending experiments.

Nikolai *et al* have proposed a five-point bending test for orthodontic archwires that is a modification of the three-point bending test. The two loading points at each end of the segment simulate the couple (equal and opposite moments) associated with engagement of the archwire in the bracket, and the fifth loading point is in the center of the wire segment. These authors point out, as have Burstone and Goldberg, that mechanical properties of orthodontic wires should be determined from plots of elastic deflection as a function of force or moment, using relevant bending tests, rather than focusing upon equations from solid mechanics. The measured bending properties should be expressed in practical units for orthodontics, such as g/mm^2 , or indexed to the property values obtained for a specific archwire size.

Figure 2.8 is a schematic illustration of the plot for the elastic range and the initial portion of the permanent deformation range from a bending test for an archwire segment (stainless steel, cobalt-chromium-nickel, and β -titanium alloys) that obeys linear elasticity (Chapter 4). The horizontal axis of the plot presents the deflection (linear or angular) as a function of

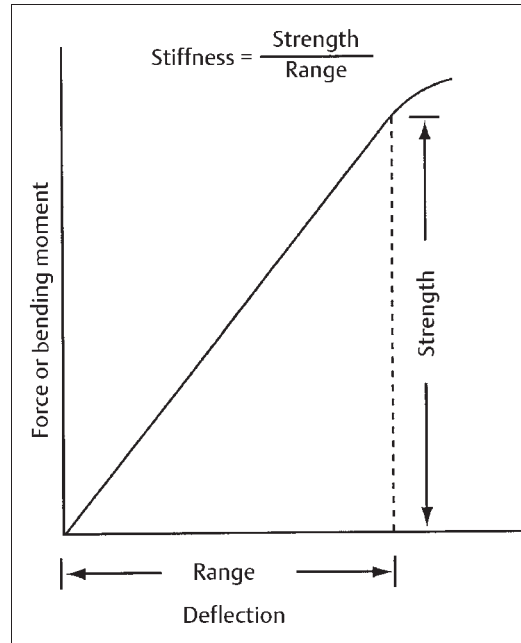


Fig. 2.8 Plot of the elastic range and the initial portion of the permanent deformation range for an archwire that exhibits linear elastic behavior in bending

the force or bending moment shown on the vertical axis.

The three clinically relevant elastic properties from this plot are: (1) the stiffness (slope of the initial linear region); (2) the force or moment at which yielding takes place (termed the strength); and (3) the value of deflection at the elastic limit (termed the range). The relationship between these elastic properties has frequently been presented in the orthodontic literature:

$$\text{Stiffness} = \frac{\text{Strength}}{\text{Range}}$$

which follows directly from the foregoing definitions and Figure 2.8. (The same relationship exists for the elastic properties of archwires determined under torsional loading conditions.) Kusy has presented nomograms of elastic property ratios, based upon this expression, linking the three major elastic properties of orthodontic archwires in bending and torsion. The property values for numerous archwires of varying cross-sectional dimensions are indexed to the properties of some reference wire, as shown

for bending of the stainless steel wires in Figure 2.9.

In closing this section, it is instructive to compare the plots in the permanent deformation range for the tension and bending tests of specimens from the same archwire. Figure 2.10 shows that the slope of the stress-strain curve is much steeper for the tension test, where the entire cross section is undergoing the same level of work hardening (Chapter 1). In contrast, when the bending deflection is sufficiently

large that the outer regions of the wire begin to undergo plastic deformation, the interior portion is still in the elastic range, which follows from the stress distribution over the cross section shown in Figure 2.2. Thus, plastic deformation in bending progresses gradually from the surface toward the center of the archwire as the amount of deflection increases. Accordingly, the slope of the bending plot in the permanent deformation range is much less steep than that for the tension test.

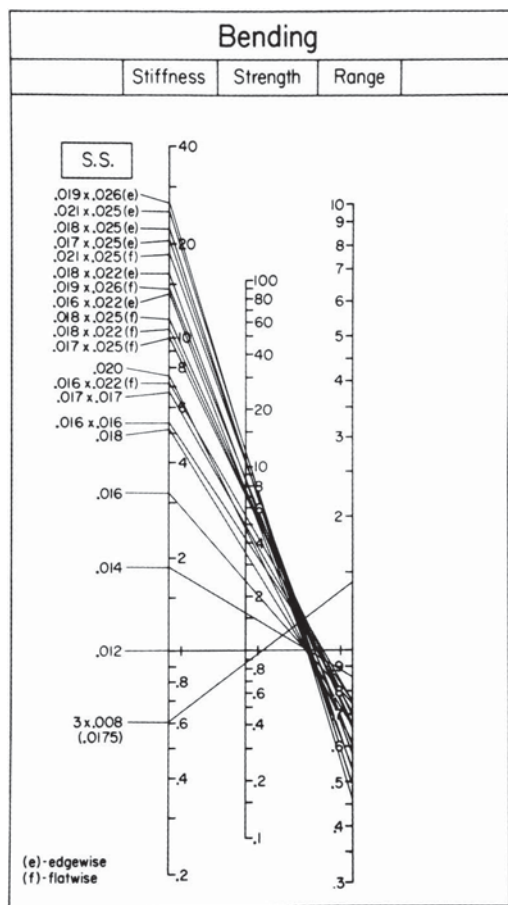


Fig. 2.9 Example of a nomogram that compares the elastic property ratios in bending for stainless steel archwires with a variety of cross-sectional dimensions. All three properties (stiffness, strength, and range) of the 0.012 inch (0.305 mm) diameter wire have been assigned a value of 1. Nomograms for archwires fabricated from other alloys, such as β -titanium and nickel-titanium, can also be indexed to the 0.305 mm diameter stainless steel wire. (From Kusy, 1983)

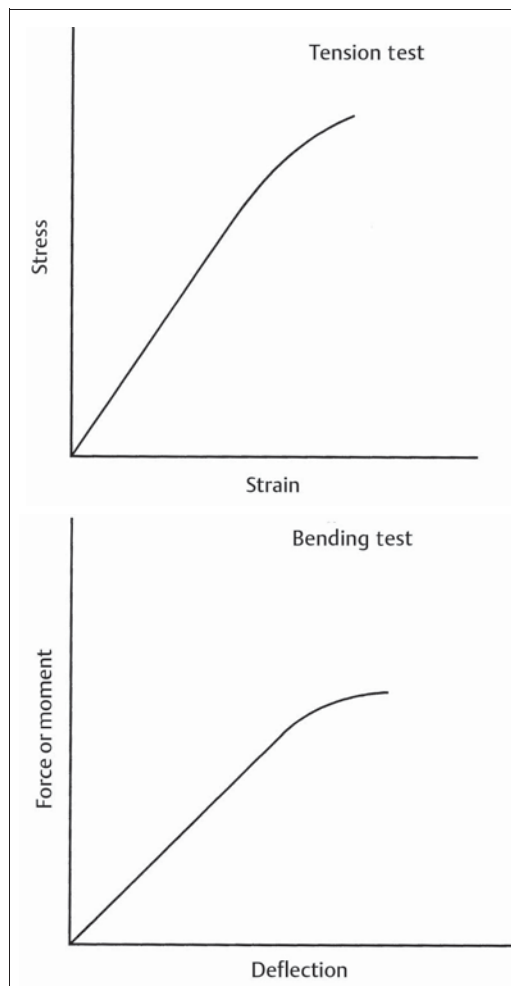


Fig. 2.10 Comparison of schematic plots for the tension and bending tests of nominally identical specimens of the same ductile orthodontic wire alloy. Note the greater slope in the permanent deformation range for the tension test

Bond Strength Measurements

One of the most active areas of orthodontic materials research is measurement of the strength of the adhesive bond between a bracket and etched tooth enamel or some other surface. Detailed information will be provided about the enamel etching, brackets, adhesives, and bonding in Chapters 5, 7, 9, 10 and 13.

Figure 2.11 provides schematic illustrations of a bracket bonded to the enamel surface of an extracted tooth and subjected to a tensile force or a shear force to cause bond failure. In the majority of published articles, a value of bond strength is calculated as the quotient of the force at which debonding occurs (determined from the load drop on the mechanical testing machine) and the interfacial area of the adhesive or bracket base. Bond strengths have been measured under tensile, shear/peel, and torsional loading.

Extensive research by Katona and colleagues, using finite-element analyses, has shown that this simple approach to the calculation of bond strength yields erroneous results. These investigators have considered the different modes of load application and the instrumental configurations for bond strength testing, and have shown that the stress distribution within the adhesive layer and the stresses generated in the brackets and enamel during testing are inhomogeneous. Stress concentrations occur, at which the local stress is considerably greater than the nominal stress based upon the applied force and interfacial area. Consequently, tradi-

tional bond strength studies are expected to substantially underestimate the actual local stress that caused the bond failure, which occurs by crack propagation through the relatively brittle adhesive and perhaps along one or both of the interfaces (bracket-adhesive and adhesive-enamel). Inferences about the relative strengths of different components in the complex bonding system, based upon visual or microscopic examination of the interfacial region, should be made with caution.

Fox *et al* have made detailed comparisons of the results from published bond strength studies, presenting differences in test configurations and experimental methodology. These investigators noted the relationship of the force application site and the bracket base surface for the bending moment generated during bond strength testing. Variability in the location of this site and the relative positions of the members of the bonding system can result in substantial differences in the measured force that causes bond failure.

At present there is no standard methodology for the evaluation of bond strength to tooth enamel or other surfaces for orthodontic adhesives. Important factors that must be considered are: (a) the method of load application, *e.g.*, tension, shear/peel, or torsion; (b) the crosshead speed of the testing machine, which is typically set at 0.5 mm/min; (c) the bracket design; and (d) the statistical analysis of the data.

Katona and Chen have suggested that long, thin wires should be selected for the loop har-

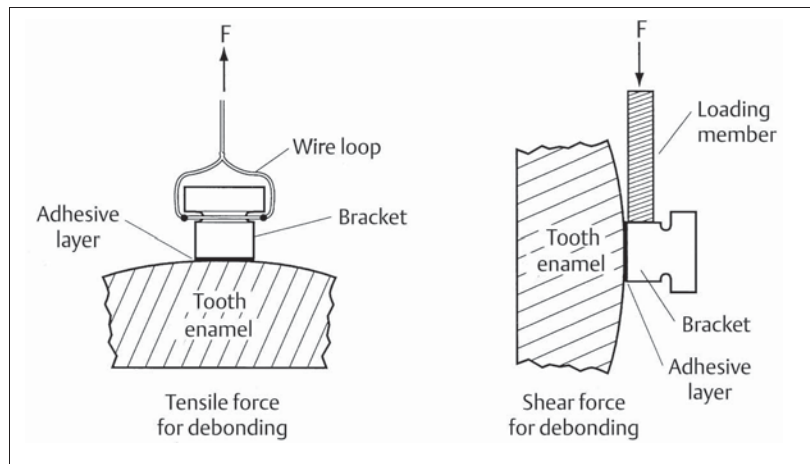


Fig. 2.11 Schematic illustrations of a bracket bonded to the enamel surface of an extracted tooth and subjected to a tensile force or a shear force

ness around the bracket wings, when this technique is employed to debond brackets by tensile loading. Better adaptation of the harness wire and lower frictional resistance with the bracket will be achieved.

While the relatively slow crosshead speed typically used for bond strength tests does allow some self-adjustment of the experimental configuration during loading, it is expected that adhesive bond failures occur at much more rapid loading rates under clinical conditions. Moreover, viscoelastic behavior that is absent *in vivo* may occur at low strain rates for the adhesive; this is an important area for future investigation.

Another factor not previously considered in the failure of orthodontic bonding systems is the possibility that cyclic fatigue processes take place in the adhesive. The major stages of fatigue involve microstructural changes that lead to the formation and propagation of microcracks to cause failure. It is possible that high-magnification scanning electron microscopic

(SEM) examination of adhesive failure sites may provide evidence of the characteristic microstructural striations (see later) associated with crack propagation during successive loading cycles. However, such detailed SEM observations of failure processes for orthodontic bonding systems may be problematic because of the presence of the bracket-adhesive and adhesive-enamel interfaces and the potentially subtle nature of any microstructural effects. It is more likely that the research emphasis will continue to be placed upon the site of final catastrophic bond failure. Nevertheless, experimental measurements of the fatigue behavior of orthodontic adhesives should be performed, along with SEM observations of the microstructures of fractured specimens.

As previously noted, it is very important in bond strength studies to consider the nature of the brackets, along with the appropriate use of units, and the type of statistical analysis. Tables 2.3 and 2.4 summarize data (based upon a published study) for a hypothetical project to

Table 2.3 Results (mean $\pm$ SD) from the shear bond strength test of three brackets bonded to enamel ($n = 10$).^a (From Eliades and Brantley, Eur J Orthod (2000); used with permission of Oxford University Press)

Measured Variable	Bracket X	Bracket Y	Bracket Z
Debonding force (N)	17.9 $\pm$ 0.9 ^a	15.2 $\pm$ 1.0 ^b	14.1 $\pm$ 0.6 ^b
Surface area of base (mm ²)	1.6	1.4	1.8
Mean bond strength (MPa)	11.4 ^a	10.9 ^a	7.8 ^b

^a Hypothetical model using arbitrarily defined force values. The bracket base area was calculated from the dimensions of representative upper incisor ceramic brackets, assuming a simple rectangular geometry.

^b Means with same letters in a row are not significantly different at the $\alpha = 0.05$ level, using the Tukey multiple range test.

Table 2.4 Significant differences among results (mean $\pm$ SD) of the debonding forces in Table 2.3, using two different multiple pairwise comparison tests. [From Eliades and Brantley, Eur J Orthod (2000); used with permission of Oxford University Press]

Bracket Type	Mean $\pm$ SD (N)	Tukey Grouping	Duncan Grouping
X	17.9 $\pm$ 0.9	a	a
Y	15.2 $\pm$ 1.0	b	b
Z	14.1 $\pm$ 0.6	b	c

F-ratio from ANOVA: 42.9.

^{a,b,c} Means with the same letters in a column are not significantly different at the $\alpha = 0.05$ level. Note that one multiple range test (Tukey) indicates that there is no significant difference between the debonding forces for bracket types Y and Z, whereas the other multiple range test (Duncan) indicates that the debonding forces are significantly different for these two bracket types.

investigate the shear bond strength for three brands of ceramic brackets to upper incisor enamel surfaces, using a chemically cured orthodontic adhesive. The sample size, debonding force, and surface area of the bracket base (assumed for simplicity to be rectangular) are shown in Table 2.3. The values of bond strength have been calculated as the quotient of the debonding force and the area of the bracket base, thus neglecting any stress concentrations.

The discrepancy in Table 2.3 between the statistically significant differences found for debonding forces and mean bond strengths may be attributed to several factors: (1) The surfaces of the bracket bases in contact with the adhesive deviate from an idealized rectangular shape. (2) There are variations in stress concentrations associated with the three brackets because of differences in morphology and interfacial characteristics of the bracket-adhesive complex. (3) Significant differences in adhesive thickness can occur for smooth and rough bracket bases, resulting in inhomogeneous load application during testing. (4) When several adhesives are tested with the same group of brackets, differences in rheological properties of the adhesives can lead to variation in the amount of microstructural porosity that is expected to be important for brittle failure.

Consequently, it is recommended that debonding force rather than stress should be reported as a measure of the bond quality when several adhesives are being compared in an *in vitro* study. Dickinson and Powers found that the bond strength was independent of the nominal base area and mesh size for 14 types of metallic brackets (although the bond strength was affected by damage from spot-welding the bracket to the base). Katona has noted a problem for comparing torsional bond strength, which is expressed in units of N/m as the quotient of torque ($N \times m$) and area (m^2), with shear bond strength expressed in units of N/m^2 .

Lastly, considering the outcome of the statistical analysis, Table 2.4 shows that different results are found with the use of two multiple range tests (Duncan, Tukey) after one-way analysis of variance (ANOVA) to compare the mean debonding forces for the three types of ceramic brackets in Table 2.3. While the appropriate sample size for bond strength testing

has been a matter of debate, as pointed out by Fox *et al*, the correct approach is to establish the optimum sample size by performing a power analysis on preliminary experimental data, using suitable α and β levels.

Measurement of Fracture Toughness

Basic concepts of fracture toughness have been presented in Chapter 1, where it was noted that fracture toughness is a measure of the force or energy for crack propagation. Several experimental methods have been used to measure the fracture toughness of brittle dental materials such as composite resins, dental ceramics, and glass ionomer cements. These methods have included the Vickers indentation technique, the single edge-notch technique, the compact tension-specimen technique, the short-rod technique with a chevron notch, and the double-torsion technique.

The three crack-opening modes that can be employed in fracture toughness tests are shown in Figure 2.12. For the crack-opening mode I, there is a tensile stress perpendicular to the face of the crack. In the forward-shear mode II, a shear stress is applied perpendicular to the leading edge of the crack and in the plane of the crack. Mode III is the parallel-shear mode, in which the stress is applied parallel to the leading edge of the crack.

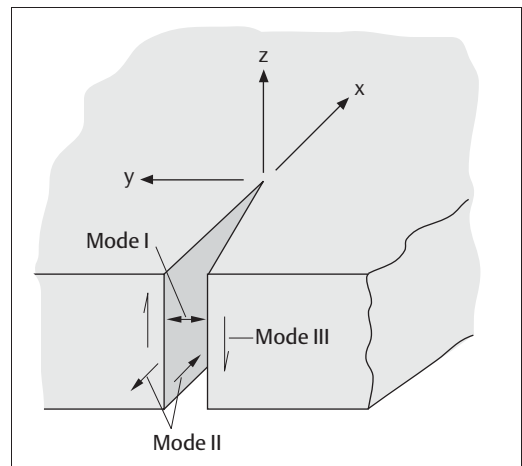


Fig. 2.12 Three crack-opening modes used in fracture toughness tests. (From Dieter, 1986)

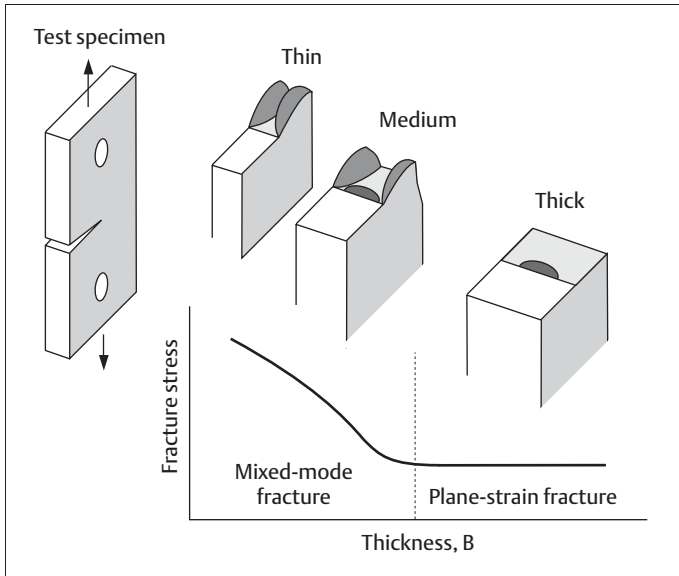


Fig. 2.13 Dependence of fracture stress, fracture mode, and general appearance of the fracture surface on specimen thickness. (From Dieter, 1986)

For mode I loading, appropriately thick specimens are required in order to have the desired plane-strain conditions. Thin, plate-type specimens will be subjected to plane-stress conditions during fracture toughness testing. (Plane strain and plane stress refer to two-dimensional states of strain and stress, respectively, and are discussed in textbooks on solid mechanics.) Plane strain represents a more severe stress state than plane stress, and the values of fracture toughness are lower for plane-strain conditions. Figure 2.13 illustrates the dependence of fracture stress, mode of fracture, and general appearance of the fracture surface on the specimen thickness. It can be seen that, once the thickness exceeds a certain value, plane-strain conditions exist and the fracture stress is constant. Hence, the plane-strain fracture toughness is considered to be a fundamental material property, similar to the modulus of elasticity.

For dental materials, mode I fracture toughness testing is generally performed, and K_{Ic} is measured. The symbol K refers to the stress-intensity factor and is an important term in equations from solid mechanics that describe the local stress distribution around the crack tip. The value of K depends upon the nominal stress for the test specimen and both the crack and specimen geometry. The symbol I corresponds to mode I testing, and the symbol c

corresponds to the critical value of K for crack propagation. For a sharp crack of length ($2a$) in an infinitely wide plate, the basic equation is

$$K_{Ic} = \sigma_F \sqrt{\pi a}$$

where σ_F is the fracture stress of the material. Consequently, the mean length of the Griffith flaws in brittle materials (Chapter 1) can be estimated from measurements of fracture toughness.

The Vickers indentation technique is particularly useful for measuring the fracture toughness of small specimens, and this method has been used to obtain the fracture toughness of alumina and zirconia brackets, as noted in Chapter 1. The brackets are embedded in metallographic resin, and the bases are polished using a series of abrasives, finishing with a sub-micrometer diamond paste. The Vickers hardness testing machine is used to place an indentation on the polished specimen surface. The length of the cracks emanating from the corners of the indentation (Figure 1.26) are used to determine the fracture toughness (K_{Ic}) from the relationship

$$K_{Ic} = 0.016 (E/H)^{1/2} (P/c^{1/2})$$

where E is the modulus of elasticity, H is the Vickers hardness, P is the load applied to the indenter, and c is the average distance of the crack tip to the center of the indentation. Because ac-

curate values of E are not generally available, the technique described by Rosenstiel and Porter is highly useful to determine the ratio of E/H . The ratio of the lengths of the diagonals for the Knoop hardness indentation (Chapter 1) on the specimen surface are compared to those for the Knoop diamond indenter.

To obtain accurate values of fracture toughness with the Vickers indentation technique, it is essential that the indenter is perpendicular to the specimen surface and that the crack lengths are measured immediately after indentation, using the microscope attached to the hardness tester. The optimum indenting load will produce cracks having a length equal to or greater than the diagonal of the indentation. Semielliptical Palmqvist cracks occur in a small, shallow plastic deformation zone beneath the indentation when the load is too light, and lateral chipping is evident when the load is excessive. Errors in the determination of K_{Ic} can occur if the measurement of crack length is delayed, owing to the likelihood of significant crack growth with time. The cracks emanating from the corners of the indentation should be straight, since the relationship for fracture toughness is based upon a microscopically homogeneous, isotropic material (such as a glass microscope slide, which serves as an excellent control for these experiments). It has been found that the desired straight cracks are essentially obtained with indentations in zirconia brackets, which have a submicrometer grain size. However, this may not be the case with polycrystalline alumina brackets, where cracks appear to follow grain boundaries.

The single edge-notch technique has also been popular for measuring the fracture toughness of a variety of dental materials. A rectangular bar specimen is prepared, having a test span length S between the two supports, a width W , a breadth B , and a centrally located notch of length a , as shown in Figure 2.14. There are several dimensional requirements in the ASTM (American Society for Testing and Materials) standard for the test specimen: the W/B ratio is 2; the a/W ratio must be between 0.45 and 0.55; and the values of both a and B must exceed $2.5 \times K_{Ic}/(YS)^2$, where YS is the yield strength (elastic limit or fracture stress for a brittle material). In many studies where the single edge-notch technique was used, the notch was molded (e.g., with a razor blade

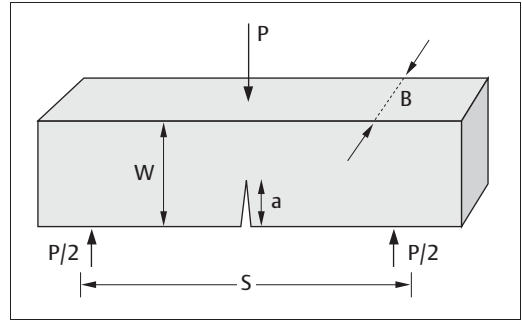


Fig. 2.14 Specimen for the single edge-notch technique used to measure fracture toughness. (From Mante et al, 1993)

or a sharp plate) or cut (e.g., using a disk with a dental handpiece) into the specimen. The basic premise has been that there will be a myriad of potential Griffith flaws at the tips of such relatively large cracks. However, the proper procedure is to first create a starting crack, subject the specimen to cyclic fatigue loading to obtain a sharp extension of this initial crack (recommended in the ASTM standard), and then measure the resulting total crack length (a) with a microscope. For the single edge-notch technique, the equation for fracture toughness is

$$K_{Ic} = \frac{PS}{BW^{3/2}} f\left(\frac{a}{W}\right)$$

where f is a function of the ratio a/W whose values are given in the ASTM standard, and P is the load at which specimen fracture occurs.

It is very important with use of the single-edge notch technique that the specimen dimensions are appropriate for plane-strain conditions. The requirements that a and B must exceed $2.5 K_{Ic}/(YS)^2$ and the typical geometry of $S = 4W$ result in relatively large test specimens, which may have excessive amounts of porosity or other flaws compared to those normally found in specimens more nearly the size of typical dental restorations. The compact tension-specimen technique has the advantage of smaller specimen dimensions that still meet plane-strain requirements.

Fujishima and Ferracane have compared the values of K_{Ic} for posterior composite resins, using the single edge-notch technique, the compact tension-specimen technique, the short-rod technique, and the double-torsion technique. Schematic illustrations of the speci-

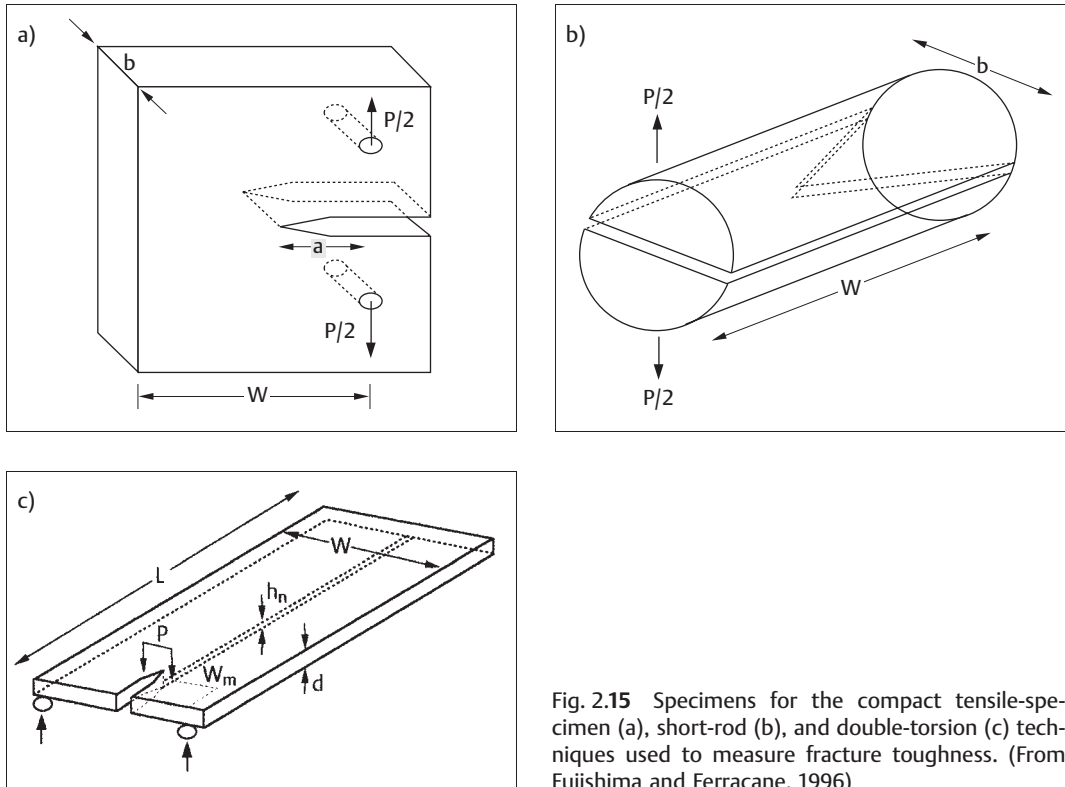


Fig. 2.15 Specimens for the compact tensile-specimen (a), short-rod (b), and double-tension (c) techniques used to measure fracture toughness. (From Fujishima and Ferracane, 1996)

men geometry for the latter three test methods are presented in Figure 2.15. The values of K_{Ic} were generally lower for the double-tension technique, which yielded the most information about crack initiation and propagation. While this test may provide the most indicative values of fracture toughness for composite resins, it was found to be highly technique-sensitive and difficult to conduct, with only half of the specimens being tested successfully. The values of K_{Ic} obtained from the short-rod test were significantly higher than those from the other three tests, and examination of the load-deflection curves and fracture surfaces suggested that a stable crack-growth region with valid test results could not be achieved.

Diametral-Compression Test

The diametral-compression test is very useful for measurement of the tensile strength of brittle dental materials, such as resins and cements, where specimens would fracture in the grips used for the conventional tension test. A second

advantage is that small disk-shaped specimens are prepared that have dimensions comparable to those for a restoration and thus may not have the substantial amount of porosity often found in larger test specimens. Because of its potential importance for evaluating the tensile strength of many orthodontic materials, a brief summary of this test is provided in this section.

As described in Chapter 1, during this test a compressive load is applied along the diameter of a round specimen, and the transverse tensile strain causes the specimen to fracture into two halves. In some cases, each of the specimen halves is further fractured into two fragments, yielding a triple cleft fracture. The relationship between the diametral tensile strength (DTS) σ and the applied load P is

$$\sigma = \frac{2P}{\pi dt}$$

where d and t are the diameter and thickness of the test specimen, respectively. The solid mechanics model assumes that the specimen undergoes only elastic deformation with com-

pletely brittle fracture, although some investigators have used the diametral compression test to determine a tensile strength for materials that experience limited permanent deformation.

From their mechanics analysis, Rudnick *et al* strongly recommend the use of padding to eliminate stress concentrations where the specimen is in contact with the crosshead and the load cell. In principle, the value of DTS calculated from the above relationship is independent of the aspect ratio d/t for the test specimen, so that disk-shaped (high d/t) or cylindrical (low d/t) specimens would yield the same results. However, larger specimens are expected to contain a greater number of Griffith flaws, resulting in lower measured values of DTS.

Differences have been found in the values of tensile strength for the same brittle dental material as determined with the diametral-compression test and the three-point and four-point bending tests. Further research is necessary to understand the reasons for these differences, which presumably arise from the complex states of combined stresses that exist in test specimens for all three of these tests. Another factor may be the locations of microstructural porosity and other constituents in the test specimens, which have considerably different geometry for the diametral-compression test and the bending tests.

Measurement of Fatigue Behavior

Traditionally, fatigue tests for engineering materials have involved cyclic loading conditions, in contrast to the single loading (and sometimes also unloading) cycle used in other laboratory tests to evaluate the mechanical properties of materials. Methods for cyclic fatigue tests are described at length in textbooks on the mechanical behavior of materials. Specimens have been tested in a wide variety of loading regimes that include tension, compression, flexure, and torsion, using sinusoidal and other waveforms for the cyclic conditions. The loading conditions used in the laboratory should mimic the conditions that the specimens being tested would experience in their normal service environment.

For the standard fatigue experiments on metals where a high number ($> 10^5$) of test cycles are performed, S - N curves, as shown in Figure 2.16, are plotted that portray the relationship between stress (S) and the number of cycles (N) to failure. The S - N curve is determined for a specified value of mean stress, ratio of maximum and minimum stress, or ratio of the alternating and mean stress. Figure 2.16 shows that for certain metals the S - N curve becomes horizontal at some value of stress (fatigue limit), below which failure is not expected to occur. Other alloys do not display such a fatigue limit, and the stress for failure becomes progressively lower with an increasing number of test cycles. In this case, a value of stress for the fatigue limit must be specified for a particular number of cycles (termed the runout).

The measurement of fatigue properties has been of considerable importance for orthopedic implants, and minimum values of the fatigue limit for these implant alloys are specified in the ASTM standards. For both prosthodontic and orthopedic implant alloys, laboratory fatigue tests should exceed 10^6 cycles to provide clinically relevant information, so that the cycling rate and load-controlling capabilities of the mechanical testing machine become highly important factors. As an example, a testing rate of 10 Hz will yield nearly 10^6 cycles in one day (8.64×10^5 cycles). The investigator must be cautioned that increasing the frequency of cycling may cause significant temperature in-

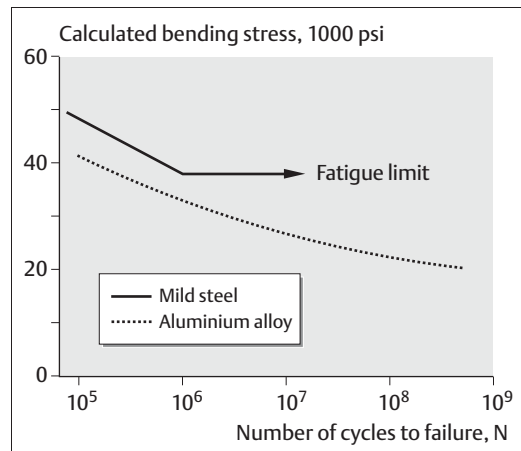


Fig. 2.16 S - N curves for two alloys, illustrating the cases of a fatigue limit and no fatigue limit. (From Dieter, 1986)

creases and changes in the mechanical behavior of the specimen being tested.

Because the accurate determination of an S - N curve requires a large number of specimens, the cyclic fatigue limit of an alloy or other material is often determined for a specified runout using the staircase method (Fig. 2.17). Examples of this method with the appropriate equations for statistical analysis of the fatigue data are presented in the articles by Aquilino *et al*, Braem *et al* and Draughn. Preliminary experiments are first performed to estimate the fatigue limit for the specified number of cycles, and then successive specimens are tested at constant lower or higher stress increments that depend upon the whether the previous specimen failed or not at the given stress. Approximately 15 specimens (after preliminary testing) are required to determine the fatigue limit with this method.

Microscopic examination of the surfaces of alloys that have failed in cyclic fatigue typically reveal the presence of striations that correspond to incremental movement of the crack front during each cycle. Dainty has described an ingenious technique where a small number of much higher stress-amplitude cycles are periodically imposed to create marker blocks on the fracture surface. The fatigue crack propagation rate can be determined from SEM observations, where the distance between the marker blocks is divided by the time interval between load cycles (reciprocal of the cycling rate).

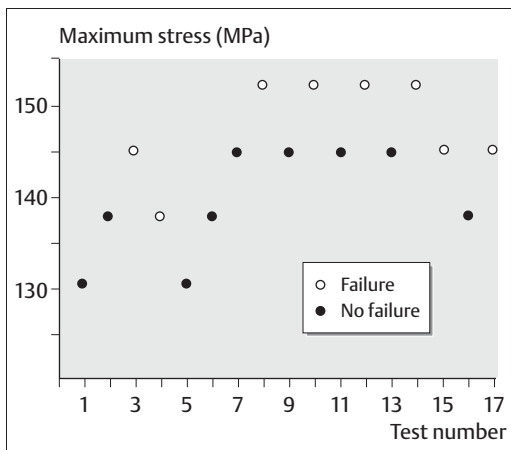


Fig. 2.17 Illustration of the use of the staircase method to determine the compressive fatigue limit of a composite resin. (From Draughn, 1979)

Static fatigue experiments have been performed on dental ceramics, where exposure to moisture causes a decrease in strength with time, due to hydrolytic attack of the Si-O structure (Chapter 1). Accelerated attack occurs at the tips of flaws in the ceramic when stress is present, and this process is referred to as a type of stress corrosion. Although not formally classified as fatigue, hydrolytic degradation also occurs in composite resins that experience prolonged exposure to water.

From the preceding discussions, it follows that two different approaches can be employed for fatigue testing: (a) In the total-life approach, the goal is to characterize the stress or strain range required for the crack initiation and propagation that result in failure. (b) The defect-tolerant approach seeks to characterize the microscopic defects that necessarily exist in the test specimen and to predict the number of fatigue cycles or time required for the dominant

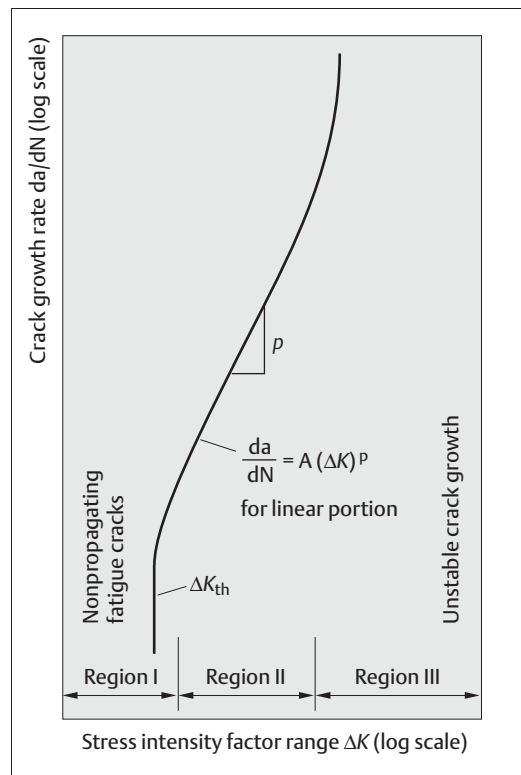


Fig. 2.18 Schematic illustration of the three regions of the fatigue crack growth rate as a function of the range in stress intensity factor. (From Dieter, 1986)

crack to grow to a critical dimension and cause failure. Equations for the fatigue crack growth rate (da/dN) during the major stage II, where well-defined crack growth takes place on planes normal to the direction of tensile loading, are presented in the textbook by Dieter. Figure 2.18 shows a schematic plot of the crack growth rate as a function of the range in the stress intensity factor (K) during the fatigue cycle.

Future studies of the fatigue behavior of orthodontic materials are highly recommended, particularly to evaluate the performance of archwires and adhesives. Research by Pruett *et al* indicates that rotary nickel-titanium endodontic instruments are susceptible to fatigue failure under dynamic flexural conditions, and studies comparing the static mechanical properties and dynamic fatigue characteristics of nickel-titanium archwires would be worthwhile. A protocol can be developed

to evaluate the fatigue properties of orthodontic adhesives that would be similar to the approach employed by Aquilino *et al* to determine the tensile fatigue limits of prosthodontic adhesives. Information from such a study is needed to allow examination of the hypothesis that fatigue processes may have a significant role for the *in vivo* failure of orthodontic adhesives.

A closing comment is worthwhile for new investigators who are beginning to employ mechanical testing in their research studies and for clinicians who are reading research articles with the objective of applying the results to their materials selection and manipulation. It is essential that these individuals understand the basic concepts of mechanical properties, know the major aspects of mechanical testing procedures, and follow the appropriate scientific approaches in interpreting experimental results.

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3 Instrumental Techniques for Study of Orthodontic Materials

George Eliades

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Secondary electron image (SEM) of a retrieved stainless steel orthodontic wire covered by intraoral integuments

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Introduction

Current advances in analytical instrumentation offer powerful tools for the study of orthodontic biomaterials and for the characterization of tissue-material interactions. The introduction of computer-controlled systems has greatly expanded the use of various spectroscopic methods in the field, providing important information for the elemental, molecular, and structural characteristics of biomaterials. Moreover, a variety of techniques have been developed for studying material surfaces and interfaces, which dominate the expression of the biological response to biomaterial properties *in vivo*.

This chapter will discuss the analytical techniques of X-ray fluorescence spectroscopy and microanalysis, X-ray diffraction, electron probe microanalysis, Auger electron spectroscopy and scanning Auger microprobe, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, Fourier transform infrared spectroscopy, Raman microspectroscopy, and differential scanning calorimetry. The fundamental principles, experimental procedures, and advantages and limitations of each technique will be presented. Examples of their application to the study of orthodontic materials will be provided.

The objective of this chapter is to present information at a level that is suitable for individuals in orthodontic materials research who are beginning to use these techniques or who need to communicate with laboratory personnel who operate the instrumentation. Other readers should find this information useful for a better understanding of research articles describing studies that have employed these techniques. More detailed presentations are available in the textbooks and other references listed at the end of this chapter.

Of the various types of spectroscopic methods available in integrated commercial systems, the most common and versatile are X-ray spectroscopy, photoelectron spectroscopy, ion spectroscopy, and vibrational spectroscopy. These techniques are dependent upon the nature of the target's response to the incident probe. Some of these methods simultaneously provide structural identification images. The depth of analysis obtained with these methods varies from a monolayer fraction (< 0.1 nm) up to many micrometers, according to the type of the radiation probe and the target used. Methods employing particles of high-energy radiation require high-vacuum or ultrahigh-vacuum environments to achieve undisturbed primary beam emission and secondary beam detection and to avoid surface contamination from the atmospheric environment. The use of high-energy probes in a high-vacuum environment has raised important questions about the relevance of these methods in studying hydrated specimens or tissue-biomaterial interfaces. Excessive drying may lead to molecular reorientation phenomena; radiation damage may alter the target composition; ion-induced destructive depth profiling may intermix target elements; and electrostatic charging may result in a severe spectral distribution for insulators. For all these reasons, the complementary use of techniques suitable for analysis of hydrated specimens has been advocated. In the present chapter a review of the spectroscopic methods used in characterization of orthodontic biomaterials is presented, aiming at better understanding the principles, procedures, advantages, and limitations of each one.

X-ray Fluorescence (XRF) Spectrometry

When an atom of an element is bombarded by X-rays of sufficient energy, inner-shell electrons absorb energy and are ejected, producing atomic vacancies; this phenomenon is known as the photoelectric effect. The excited atom then relaxes to the ground state by transition of outer

orbital electrons that fill the inner-shell vacancies. Characteristic X-rays are produced that correspond to the atomic energy loss to the excited element and are annotated by the orbital where the original vacancy was created (*e.g.*, Cr K α). Since the X-rays produced are independent of

the chemical environment of the atoms, they are suitable for elemental analysis. X-ray emission may be produced by electron beams, charged particles, X-rays, or radioactive isotopes.

The most practical energy source for X-ray fluorescence (XRF) spectrometry is an X-ray tube. Tubes do not require high vacuum or conductive samples as do electron beams, nor accelerators as does particle-induced X-ray emission, and with a single source many elements can be excited efficiently, unlike isotopic sources where more than one source is required. Selection of the X-ray tube anode material should be made so that the characteristic lines emitted by the anode are close to, but always of higher energy than, the absorption energies of the elements of interest, without creating spectral interferences. In quantitative standardless applications where monochromatic radiation is required, filters can be used with the primary radiation from the X-ray tube so that essentially only characteristic lines of the tube anode are transmitted.

Elemental identification in XRF spectrometry is accomplished by spectrometers that resolve the spectral lines emitted into separate components. There are two types of spectrometers that are available: (1) in wavelength-dispersive spectrometry (WDS) the X-rays emitted are dispersed into specific wavelengths by the mechanical movement of analyzing crystals attached to a goniometer and detected by proportional or scintillation counters; (2) in en-

ergy-dispersive spectrometry (EDS), semiconductors are used to create signals proportional to the X-ray energy. The WDS systems demonstrate higher resolution, higher-sensitivity detection, and higher counting rates than the EDS ones. However, owing to single-channel detection they are slow, and because of the goniometer arrangement they are very sensitive to topographical features. EDS is very fast because of multichannel detection and provides simultaneous multi-element analysis capability, although not all elements can be determined in every sample under the same conditions. The voltage of the X-ray tube is critical for the excitation of the elements in both WDS and EDS, and should be set higher than the absorption edge of the elements probed. The range of accelerating voltage for WDS is 0–100 keV, while for EDS the range is 0–40 keV. The tube current affects only the X-ray photon flux and thus the count rate. XRF spectrometers can operate with the sample chamber kept at atmospheric conditions, under vacuum or under helium. Generally, for detection of X-rays below 5 keV, vacuum or helium purging is required.

XRF spectrometry can be applied non-destructively to the analysis of solid samples of various forms (bulk, powders, and briquets), liquids, thin films, and filtered aerosol samples (Fig. 3.1). The technique can detect elements with atomic number $Z > 11$. Oxygen and fluorine can be semi-quantitatively measured using

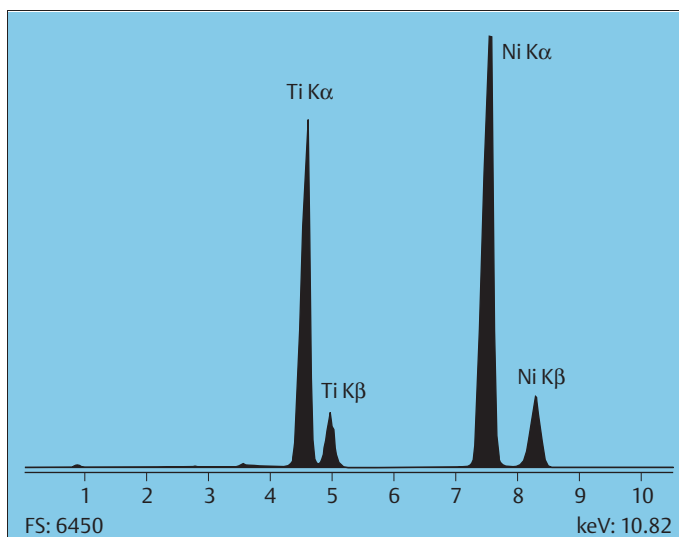


Fig. 3.1 Energy-dispersive X-ray fluorescence spectrum of a nickel-titanium orthodontic wire

special crystals or detectors. Detection limits for bulk determinations are typically from a few ppm up to a few tens of ppm, dependent on the energy used and the sample composition. For thin films, detection limits may reach 100 ng/cm².

Bulk materials may be analyzed as received since the typical sample size is 32 mm, placed in special cups or holders. For smaller samples (up to 1 mm) beam collimators are required. For quantitative determinations, precise positioning of the sample in the spectrometer is of paramount importance, especially in WDS. Samples for analysis should have a surface roughness less than 100 μm when X-rays above 4 keV are used. Care should be taken when polishing samples to avoid surface contamination, as surface smears remaining may affect the intensities of the emitted X-rays. Intense polishing grooves may lead to the same effect as well, but this artifact is minimized when sample spinners are available or when the incident X-rays are parallel to the polishing direction. Powders may be analyzed by using sample

spinners to neutralize any particle size effects from the absorption of the incident and emitted X-rays within the particles, especially at low energies. If no spinners are available, pellets prepared from pressed powders in the presence of organic binders may be used. However, the powder particle size should be less than 100 μm , otherwise grinding is advised. For analyses of refractory materials, casting the powder into a glass button avoids limitations associated with powder specimens.

The depth of analysis in XRF varies from few micrometers to a millimeter or more, depending on the X-ray energy used and the nature of the target. A growing application of XRF is in measuring film thickness and composition of coatings. Several techniques have been developed, such as the substrate intensity attenuation method, the coating intensity method, and the various intensity ratio methods for rapid on-line measurement of film thickness. Results with submicrometer accuracy can be obtained with the use of appropriate sets of standards.

X-ray Fluorescence (XRF) Microanalysis

Developments in the field of X-ray capillary waveguides allow microfocusing of X-ray beams at areas approximately 100 μm in diameter with the aid of an incident light optical microscope, thus introducing energy-dispersive XRF spectrometry in the field of microanalysis. The area of analysis is identified optically and is rapidly analyzed without the need for specimen preparation, dehydration, and appli-

cation of a conductive coating. Samples may be analyzed in atmospheric conditions, under low vacuum, or under helium purging. Although the spatial resolution of XRF microanalysis is poor and the depth of analysis greater compared with electron probe microanalysis, the flexibility of the technique and the minimal requirements for sample preparation offer unique advantages in studying hydrated specimens.

X-ray Diffraction (XRD)

X-ray diffraction (XRD), which is used to study the crystal structures of materials and related matters, is one of the major traditional laboratory tools employed in materials science. Figure 3.2 shows a beam of parallel X-rays that are incident upon atomic planes at the surface of a crystalline material. If the difference in path length for X-rays reflected from adjacent planes is an integral number of wavelengths, these reflected X-rays will be in phase and produce a strong signal at some

detector. In order for this constructive interference to occur, the interplanar spacing (d), angle of incidence (θ) and X-ray wavelength (λ) must be related by Bragg's law:

$$n\lambda = 2d \sin \theta$$

The diffraction angle (2θ) is the angle between the incident and transmitted X-ray beams. The number of wavelengths in the path length difference is designated by n , which is termed the order of diffraction.

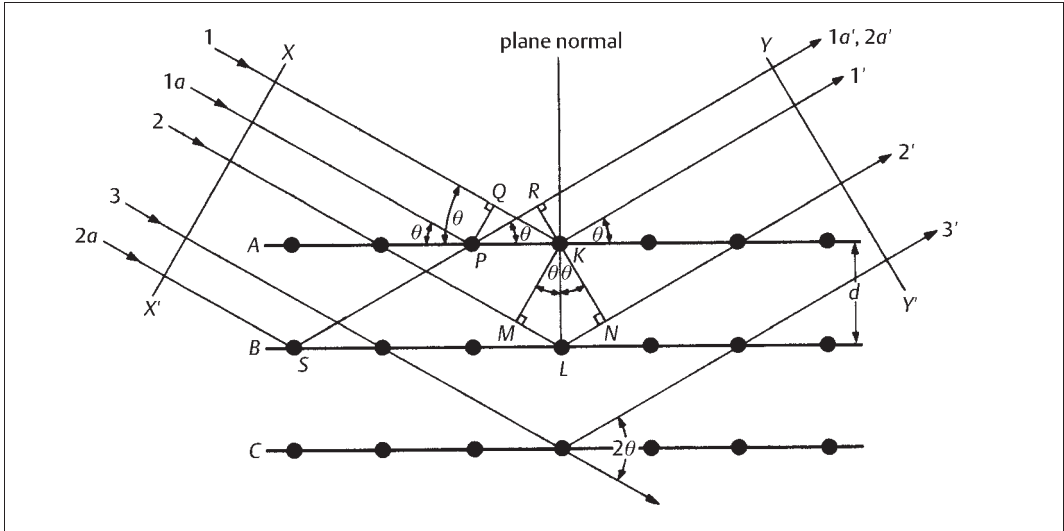


Fig. 3.2 Diffraction (reflection) of a set of parallel X-rays at the surface planes of a crystalline material. (From Cullity, 1978)

In the customary XRD methodology for orthodontic materials, nearly monochromatic characteristic X-rays, such as Cu $K\alpha$ radiation, are used. As described earlier, characteristic X-rays are generated when the accelerating voltage in the X-ray tube is sufficiently high (typically > 10 kV) that the electrons, created by passing a current (typically > 10 mA) through a filament, have the necessary energy to knock out core electrons from the K level (innermost shell) of the target metal. The most likely transitions are for electrons from the L shell to fill the vacancies in the K shell, with the creation of $K\alpha$ X-rays. However, the K shell vacancies can also be filled by electrons from the M shell, which results in the emission of $K\beta$ X-rays. (Transitions from other shells to the K shell can also occur, but these do not make a significant contribution to the beam from the X-ray tube.) An appropriate filter material or a crystal monochromator is used to greatly reduce the intensity of the $K\beta$ X-rays, so that nearly monochromatic $K\alpha$ X-rays are used for XRD analyses. Details of operation of the X-ray tube and the use of filters and monochromators are provided in textbooks on X-ray diffraction.

In the usual experiments, a polycrystalline specimen in flat plate form or a polycrystalline powder specimen is analyzed. In XRD studies of archwires, a series of parallel wire segments

may be placed in contact to obtain an acceptable specimen for the diffractometer. Figure 3.3 shows that the diffracted X-rays from an atomic plane in a polycrystalline powder specimen form a cone when the powder contains a very large number of randomly oriented crystals. The diffracted X-rays from a powder specimen may be detected with a Debye-Scherrer camera that contains film or with a diffractometer. Plate-shaped archwire specimens used with the diffractometer will not have randomly oriented crystals (grains) because of the preferred crystallographic orientation resulting from the wire drawing process, as described in Chapter 4.

Figure 3.4 is an XRD pattern for 40 °C Copper Ni-Ti (Chapter 4) obtained with Cu $K\alpha$ radiation, which is representative of results for the polycrystalline archwire alloys. The diffracted X-ray intensity is plotted on the vertical axis as a function of the diffraction angle (2θ) on the horizontal axis. The XRD peaks for the two phases present have been indexed by comparing their positions to those in the polycrystalline powder standards for austenitic (18-899) and martensite (35-1281) NiTi, published by the International Center for Diffraction Data (ICDD) (Swarthmore, PA, USA).

The method is illustrated in Table 3.1, which presents the information provided in the ICDD

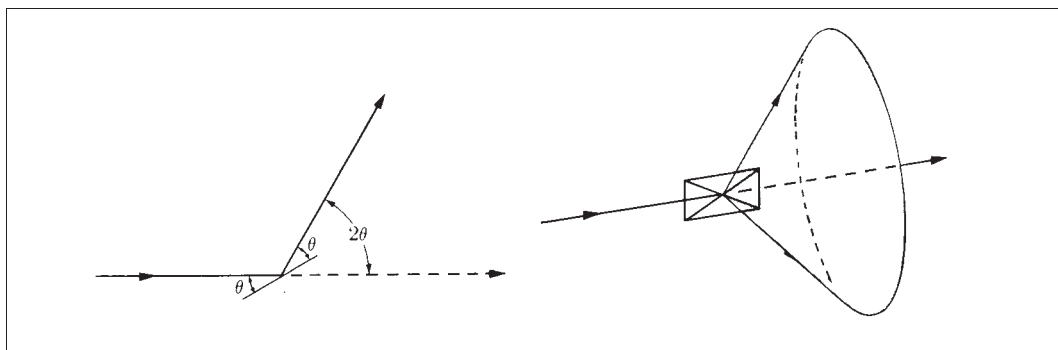


Fig. 3.3 Formation of a cone of X-rays diffracted from a powder specimen containing a large number of randomly oriented crystals. (From Cullity, 1978)

standard for bcc (modified CsCl structure) austenitic NiTi: the positions (d) of the observed XRD peaks (hkl) and their relative intensities (I). The peak positions are given as values of the interplanar spacings because the diffraction angles (2θ) will depend upon the type of X-ray

tube chosen. Tubes with many different metal targets are available, so that an investigator can select the wavelength of the characteristic radiation, such as Cu $K\alpha$, Mo $K\alpha$ or W $L\alpha$. Table 3.1 shows the successive steps for the use of Bragg's law to locate the 2θ positions of

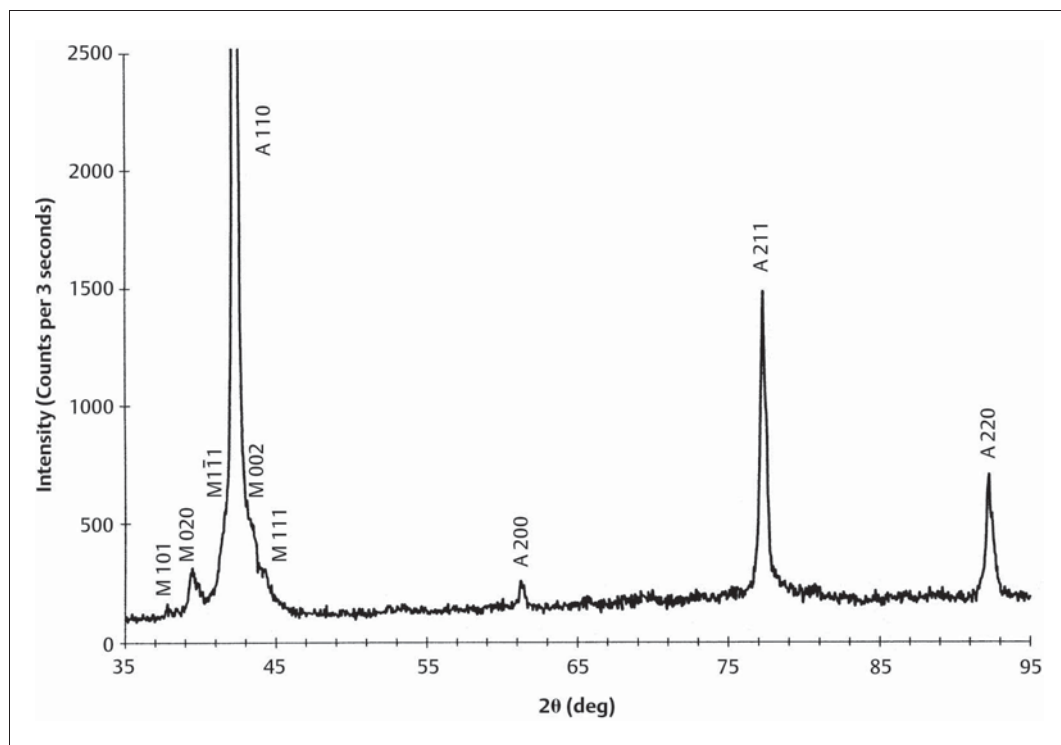


Fig. 3.4 X-ray diffraction pattern for 40 °C Copper Ni-Ti obtained at room temperature. (An abstract describing this study is found in Brantley *et al*, 1998).

the peaks for the standard when Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$ or 0.15418 nm) is employed. The relative peak intensities are normalized to the intensity for the strongest peak, which is assigned a value of 100.

Differences in observed relative intensities for the peaks in Figure 3.4, compared to values for the ICDD standard in Table 3.1, are due to the strong 110 preferred orientation of the austenitic NiTi in the archwire. Differences in the observed peak positions (2θ values or the corresponding interplanar spacings), compared to the ICDD standard, arise from incorporation of solute atom species (copper and chromium) in the crystal structure of the phase being analyzed.

For some materials the surface atomic planes giving rise to the XRD peaks can be under a state of uniform residual elastic strain. For uniform tensile strain, the interplanar spacing (d) will be increased, and consideration of Bragg's law shows that the diffraction angle (2θ) for the reflection from these planes is decreased; the diffraction angles are increased if the surface planes are under uniform compressive strain. Substantial peak broadening is often observed in XRD patterns from archwires owing to residual plastic deformation arising from the wire processing sequence, as described in Chapter 4. The peak broadening arises because the complex pattern of permanent deformation involves both tensile and compressive strains.

The hkl column in Table 3.1 represents the Miller crystallographic indices for the particular

sets of atomic planes that give rise to the observed peaks for austenitic NiTi. While a detailed discussion of the structure factor for X-ray diffraction is beyond the scope of this chapter, it can be noted that for each crystal structure (other than simple cubic) only certain sets of parallel atomic planes yield constructive interference of the reflected monochromatic X-ray beam. This series or pattern of observed XRD peaks is unique for the particular crystal structure (analogous to a "fingerprint"). When two materials, such as iron and nickel, have the same crystal structure (fcc in this case, as described in Chapter 1), the pattern of the XRD peaks is the same, although the peak positions (2θ values) differ because of the different lattice parameters.

The hkl indices are the reciprocals of the intercepts of the given atomic plane on the three crystallographic axes (conventionally termed x , y and z) for the unit cell. An index of zero means that the atomic plane is parallel to the corresponding axis of the unit cell. For example, the 310 peak in Table 3.1 is for a series of planes that intersect the x -axis at one-third of a unit (lattice parameter) and the y -axis at one unit from the origin. Because these planes are parallel to the z -axis, the z -intercept is considered to be infinity, which yields a reciprocal value of zero for the Miller index. For martensitic NiTi, which has a monoclinic crystal structure (Chapter 1), a negative crystallographic index, designated by a bar over the number, is shown for the $\bar{1}\bar{1}1$ reflecting plane

Table 3.1 ICDD standard 18-899 for austenitic NiTi (CsCl structure with space group Pm3m), showing the relative intensities (I) of the observed reflections (hkl) and the corresponding interplanar spacings (d). Additional columns for $\sin \theta$ and θ indicate the steps involved in the use of Bragg's law to determine the peak positions (2θ) for Cu K α radiation

hkl	$d \text{ (\AA)}$	$\sin \theta^a$	$\theta^a \text{ (deg)}$	$2\theta \text{ (deg)}$	I
110	2.111	0.36490	21.40	42.80	100
200	1.496	0.51491	30.99	61.98	40
211	1.222	0.63036	39.08	78.16	60
220	1.059	0.72738	46.67	93.34	10
310	0.948	0.81255	54.35	108.70	30
222	0.865	0.89052	62.94	125.88	20
321	0.8012	0.96143	74.04	148.08	70

^aFor Cu K α radiation (weighted average $\lambda = 1.5418 \text{ \AA}$ for Cu K α^1 and Cu K α^2).

Table 3.2 ICDD standard 35-1281 for martensitic NiTi (monoclinic structure with space group $P2_1/m$), showing the relative intensities (I) of the observed reflections (hkl) and the corresponding interplanar spacings (d). As in Table 3.1, additional columns for $\sin \theta$ and θ indicate the steps involved in the use of Bragg's law to determine the peak positions (2θ) for Cu $K\alpha$ radiation

hkl	d (Å)	$\sin \theta^a$	θ^a (deg)	2θ (deg)	I
1 $\bar{1}$ 0	2.570	0.29973	17.44	34.88	13
101	2.352	0.32751	19.12	38.24	11
020	2.295	0.33564	19.61	39.22	54
1 $\bar{1}$ 1	2.181	0.35319	20.68	41.36	100
002	2.060	0.37393	21.96	43.92	54
111	2.016	0.33209	22.46	44.92	94
021	2.005	0.38419	22.59	45.18	26
022	1.533	0.50248	30.16	60.32	26

^aFor Cu $K\alpha$ radiation (weighted average $\lambda = 1.5418$ Å for Cu $K\alpha^1$ and Cu $K\alpha^2$). There are 13 additional peaks with relative intensities $I < 10$. The highest-angle peak located at $d = 1.530$ Å ($I = 1$) corresponds to $2\theta = 60.46^\circ$.

in Figure 3.4. The peak positions and intensities in ICDD standard 35-1281 for martensitic NiTi are shown in Table 3.2. A negative crystallographic index for a crystal plane indicates that the intercept is on the corresponding negative axis with respect to the origin for the unit cell.

For materials containing more than one phase, such as 40 °C Copper NiTi in Figure 3.4 or some stainless steel archwires, as discussed in Chapter 4, the XRD pattern will contain the series of peaks for each phase. Some phases, such as chromium carbide in stainless steel archwires, may not have significant XRD peaks because of their composition and structure or because the amount of the phase in the microstructure is too small. For the analysis of an unknown material by X-ray diffraction, computerized search programs that are available with modern diffractometers are used to compare the strongest observed peaks with the library of ICDD standards. Indexing the peaks for a multiple-phase material where no information is available about the microstructure can be a very difficult task. Common problems are overlapping peaks from different phases and the existence of a preferred orientation that greatly alters the relative intensities of peaks from those in the ICDD standards.

X-ray diffraction is inherently a near-surface analytical technique, since the depth of penetration of the X-ray beam is typically no greater

than 50 μm and frequently much less for the metals of usual interest. Consequently, caution is necessary when interpreting the results of XRD experiments, since the near-surface structure of a material may differ significantly from the bulk structure. While such an experiment is generally very difficult to conduct, the safest procedure is to perform a series of XRD analyses on specimens from which known thicknesses of surface layers have been removed.

Most research articles in the orthodontic materials literature involving the use of X-ray diffraction have focused on archwire alloys. Recent studies have shown the applicability of X-ray diffraction to the identification of phases in zirconia ceramic brackets (Chapter 7) and to the characterization of changes in tooth enamel under clinically important conditions. Fluoroapatite formation in enamel due to fluoride release from glass ionomer cement, the analysis of enamel lesions to confirm whether fluoride was incorporated during remineralization, and the effect of gel applications on enamel crystallinity have been investigated. These topics will be discussed further in Chapters 6 and 11.

Electron Probe Microanalysis (EPMA)

In electron probe microanalysis (EPMA) an electron beam accelerated at 10–30 keV is microfocused on a small area (10 nm to 1 μm in diameter), and specimen microvolumes are excited by scanning the beam over the target. The inner-shell electrons of target atoms are ionized, and upon relaxation they emit either X-rays from a one-stage transition, as described before, or undergo radiationless two-stage transitions producing Auger electrons. X-ray emission decreases in favor of Auger emission as the atomic number decreases, and this is the main reason why Auger electron spectroscopy is more sensitive in light-element analysis. When X-ray emission occurs, the emitted X-rays can be detected by WDS or EDS, providing information about the elemental composition of material microregions. The depth of analysis depends on the accelerating voltage and the target properties. In EDS the depth is approximately 1 μm , while in WDS, which usually operates at higher accelerating voltage, the depth may exceed 5 μm . The lateral resolution is somewhat larger owing to diffuse scattering of the incident electrons. The detection limits are 0.1 % by weight for EDS and 0.01 % by weight for WDS. EPMA requires conductive specimens to avoid electrostatic charging. For the study of insulators, conductive coatings should be applied.

Modern EPMA systems are coupled to scanning (SEM), conventional transmission (CTEM) or scanning transmission (STEM) electron microscopes. Thermionic SEMs can be equipped with both WDS and EDS systems. Low-pressure and environmental SEMs, CTEMs and STEMs are mostly compatible with EDS. EPMA offers the following analysis modes: (a) point analysis, where a spectrum at a selected point is taken; (b) line scan analysis, where the elemental gradients along a linear direction are measured; and (c) area scan analysis, where the elemental distribution in the form of elemental mapping is traced. Imaging and analysis in EPMA are performed by detecting various electron signals emerging from secondary emitted electrons, backscattered electrons, and characteristic X-rays. However, since the sample volumes contributing to these signals are different, care should be taken about the correct

interpretation of the results (Fig. 3.5). Secondary electrons, providing the conventional SEM images, originate from the uppermost few nanometers. Backscattered electron images, especially from the inelastically scattered fraction, originate from a depth of hundreds of nanometers, while characteristic X-rays originate from a depth of a micrometer or more. Since the atomic number contrast of backscattered electron detectors is stronger than that achieved with the secondary electron detectors, backscattered electron images are preferred for assigning elemental distributions, especially in multiple-phase specimens. The use of backscattered electron images is most important when analyzing features with sharp edges (e.g., interfaces), because detection of the forward-scattered electrons by the secondary electron detector produces image flaring. This distortion is minimized in backscattered electron images, and clear interfaces are obtained.

As in XRF spectrometry, WDS demonstrates superior resolution to that of EDS, better sensitivity for low-atomic-number element analysis ($Z < 10$), and lower detection limits by a factor of 10–100; superior elemental distribution images (elemental mapping) will be obtained. However, WDS is more sensitive to topographical features owing to beam defocusing, needs higher vacuum and higher beam currents than EDS, and is considered more destructive to organic materials. For quantitative analysis

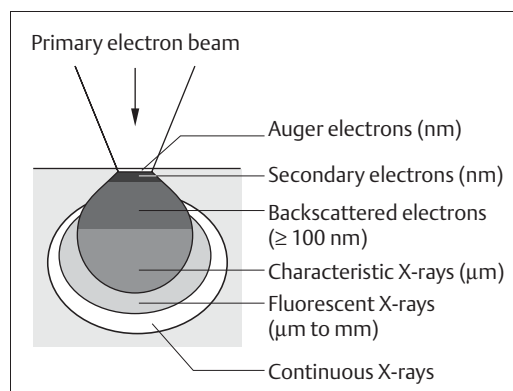


Fig. 3.5 The different depths of various information obtained from a specimen subjected to electron beam irradiation

of specimens with unknown composition, EDS offers the advantage of rapid multi-element detection. Nevertheless, WDS systems are the spectrometers of choice for resolving overlapping peaks or for the quantitative analysis of major and minor constituents. Both spectrometer types are sensitive for elements with $Z \geq 5$. The most common artifacts in qualitative analysis by EDS are the sum peaks, the escape peaks and the internal fluorescence peaks. Sum peaks are recorded at the low-energy region from major spectral components due to coincident detection. Escape peaks are produced from the photon detection process in the [Si (Li)] detector, where sometimes silicon is in an excited state emitting X-rays at ~ 1.74 keV. Internal fluorescence peaks may arise from the thin silicon layer in front of the detector. Care should be taken for peaks over 15 keV, which usually appear at low intensity because the efficiency of the detector at the high-energy region is reduced, since some X-rays can penetrate through the detector. In WDS analysis the main problem is the production of a series of peaks from the diffraction orders of the same element that appear at different angles (harmonic peaks). In the low-energy region (< 2 keV) peak shifting may occur, depending on the chemical state of the element in the sample.

Quantitative analysis in EPMA is based on the fundamental observation that X-ray intensities are directly related to the elemental concentrations. It is usually performed by data-reduction computer programs for spectral data correction. Baseline, dead time, atomic number (Z), absorption (A), and fluorescence (F) correction algorithms are generally used. Standardless analysis is considered a semi-quantitative procedure because of matrix effect interferences, although in some cases acceptable results may be obtained. The use of standards minimizes the matrix effects, resulting in low detection limits.

The most important advantage of EPMA is elemental mapping, which provides qualitative and quantitative information on the area distribution of the elements in a specimen (Fig. 3.6). There are two types of elemental mapping. In conventional or analog dot-mapping, the X-ray signal from the spectrometer is synchronized with the image display, so that an elemental distribution image of modulated bright-

ness is recorded. The concentration variations are denoted by differences in the area density of the dots. Owing to limitations in the spatial resolution of the X-rays emitted, the maximum magnification for dot-mapping should not exceed $2000\times$, otherwise overlapping of pixels may occur. For WDS the low-magnification limit is $400\times$ or more, dependent on the specimen topography, to avoid defocusing

Fig. 3.6 Wavelength-dispersive electron probe microanalysis of a retrieved stainless steel orthodontic wire covered by intraoral integuments. (a) Secondary electron image. (b) Compositional backscattered electron image. (c) X-ray image of Cl (K and Na images were similar). (d) X-ray image of S. (e) X-ray image of Ca (P image was similar). The entire region probed was covered by a partially calcified biofilm. Note the difference between secondary and compositional backscattered electron images and the intense edge-effect at the upper part of the secondary electron image



Fig. 3.6 a

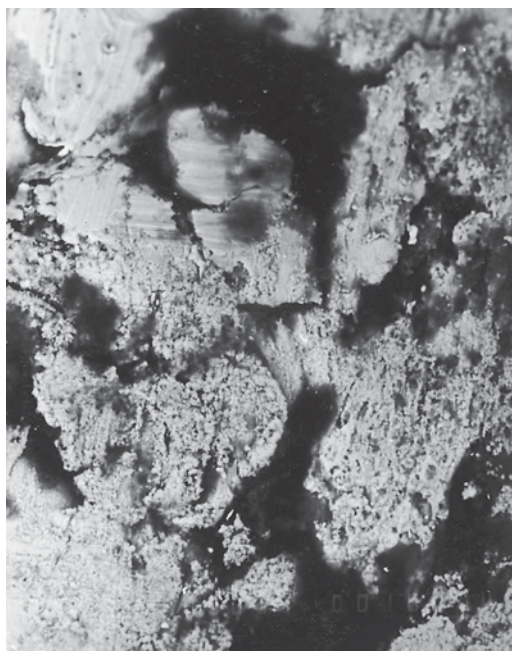


Fig. 3.6b

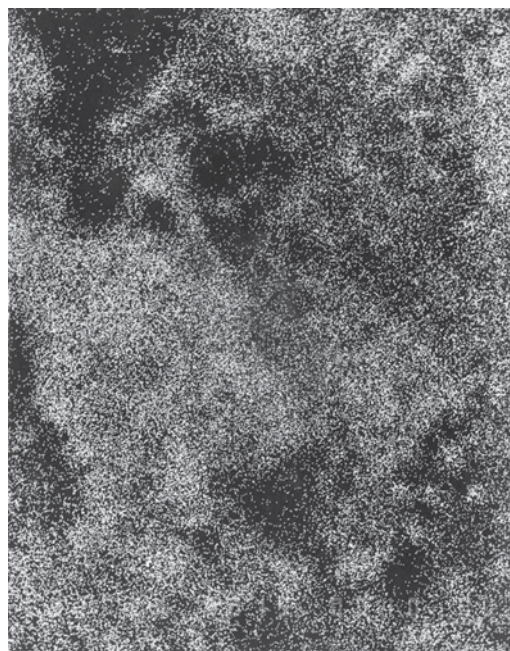


Fig. 3.6c

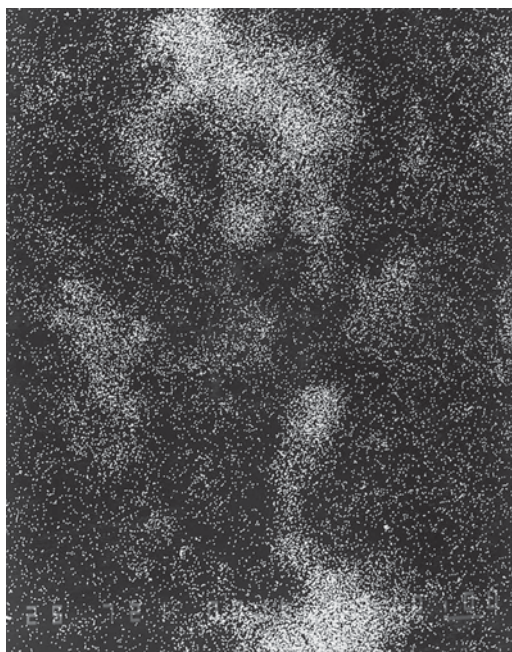


Fig. 3.6d

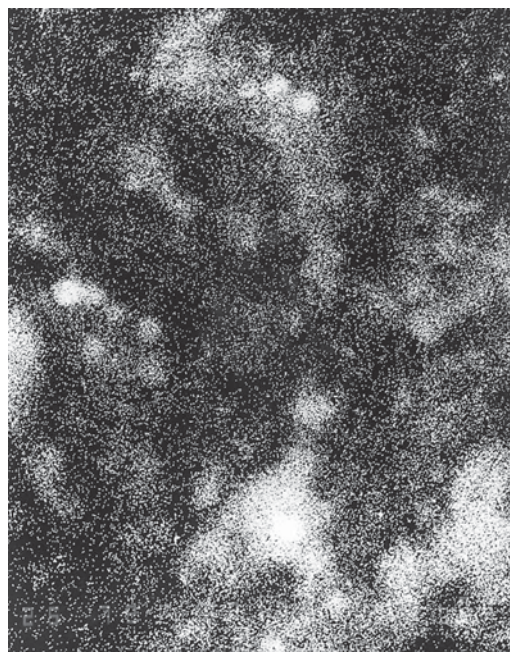


Fig. 3.6e

artifacts. WDS systems are much more sensitive in dot-mapping than are EDS ones. The latter are not reliable for elements with concentrations $< 5\%$ by weight. In digital or quantitative mapping the true X-ray counts are retained for each image pixel, and thus quantitative analysis can be performed at any point. Gray-scale or color coding may be employed to show concentration variations.

EPMA for problem solving should be used under several restrictions. EPMA should not be applied for bulk analysis, since scanning a large area to obtain an average quantitative composition results in a very high error owing to inhomogeneity of the region. In such applications the specimen should be scanned at many sites or analyzed by bulk analysis techniques such as XRF. Similar problems are faced when analyzing material sections. One section should not be considered representative of the material structure. There are several material requirements for EPMA, regarding surface roughness and conductivity. The specimen should be relatively flat without deep grooves or scratches, especially when WDS analysis is used. Polishing should be performed mechanically and not by any chemical means that may affect the chemical composition of the specimen. Any polishing artifacts such as smearing, phase extraction, or interlocking should be considered in the analysis. Specimens containing water and organic matter, like biological tissues, are very sensitive to dehydration and radiation damage, either during analysis or during exposure to the beam prior to analysis when searching the region of interest. Fixation and controlled dehydration have been recommended for the avoidance of artifacts. Nevertheless, conventional methods (e.g., glutaraldehyde, osmium tetroxide, ethanol solutions, and critical-point drying) may alter elemental distributions. The same concern applies for demineralization procedures routinely used in TEM studies. Cryogenic procedures like quench-freezing or freeze-drying offer several advantages for imaging and analysis, since no side interactions are involved. EDS is preferentially used for tissue analysis to avoid high count rates and sample currents, although the high background levels in EDS reduce the capacity for detection of minor constituents, rendering EPMA a semi-quantitative elemental analysis method.

The thickness and the quality of the conductive coating applied on insulators to avoid electrostatic charging are of primary importance for both imaging and analysis. A thin layer of graphite should be used in EPMA to avoid any interferences of the atomic number of the coating with the analysis. In some modern SEMs equipped with variable-pressure modes, imaging of the specimens is performed at low vacuum in a hydrated state, without the need for coating. However, the excitation energies are insufficient for EPMA. Analysis by EDS only is feasible, but at higher acceleration voltage that can cause beam damage to the specimens. A major problem in EPMA is the study of soft tissue-biomaterial interactions due to structural incompatibility, which creates interfacial artifacts. A typical example is the measurement of fluoride uptake by enamel bonded to a glass-ionomer cement. The fluoride uptake has been documented by WDS/EPMA studies using line scan analysis perpendicular to the interface. Nevertheless, in a recent study by Duschner *et al* employing advanced microanalytical techniques, it was demonstrated that there was no fluoride uptake by enamel and that the fluoride probed at the enamel surface was attributed to attached glass-ionomer cement microfragments. Apparently, excessive dehydration of the glass-ionomer cement under high vacuum produced material cracking and interfacial debonding, leaving adherent microfragments on the enamel, which in the EPMA analysis were considered as phases arising from elemental diffusion into enamel. In such complicated cases multi-technique characterization involving high-resolution interfacial imaging and complementary microanalytical techniques is required. EPMA coupled to SEM is the most frequently used elemental microanalysis method in dental materials research.

For CTEM-EPMA and STEM-EPMA, EDS detectors are exclusively used. These systems offer the ultimate spatial resolution as the beam diameter may be reduced to 0.5 nm. Major limitations of this method are that the sample must be an ultrathin section and that only a very small area is analyzed. The most difficult task in TEM-EPMA is specimen preparation, especially when interfaces of biomaterials and tissues are processed.

Auger Electron Spectroscopy (AES)

Generation of Auger electrons involves two-stage radiationless electronic transitions, induced by incident radiation with energy exceeding that required to remove inner-shell electrons. In such cases the excess energy after production of a core vacancy is expended toward the ejection of an electron (called an Auger electron) from a third level. Auger electron spectroscopy (AES) involves the detection and kinetic energy resolution of the Auger electrons. Primary excitation is usually performed by electron sources (0.5–10 keV) focused in a diameter of 0.1–1 mm under ultra-high vacuum (UHV), typically 10^{-10} torr. The Auger electrons produced are energy-resolved by cylindrical mirror analyzers or concentric hemispherical analyzers over an energy range of 0–2500 eV. The depth of analysis in AES is limited to the top 2 to 10 monolayers (atomic layers), which correspond to a depth of 0.5–3 nm, independently of the primary electron energy used. All elements are detected in AES, with the exception of H and He, since at least three electrons are required to generate an Auger electron. The detection sensitivity for most elements is 0.01–0.1 at%. The Auger signal yield is higher for low-atomic-number elements ($Z < 11$), resulting in high sensitivity of AES for light-element analysis. The kinetic energy of the characteristic Auger electrons is dependent on the chemical environment of the electrons, and thus AES can be used for identification of the chemical state of surface atoms participating in ionic bonding and oxidation. Quantification of AES is quite difficult and should be based upon standards. For materials with no or limited chemical effects, the accuracy of the quantitative determinations is within $\pm 10\%$. Standardless methods have limited accuracy ($\pm 30\%$).

AES analysis is usually combined with secondary electron images of the regions of interest, providing elemental mapping or compositional gradients (Fig. 3.7). However, when improved spatial resolution is required, the scanning Auger microprobe (SAM) should be used. AES may provide in-depth compositional information, either by nondestructive angle-resolved depth profiling or by destructive ion-induced depth profiling. In angle-resolved analy-

sis the specimen is rotated so that the analyzer receives electrons from increasing angles corresponding to fractions of the original depth of analysis. In ion depth profiling, Ar^+ ions accelerated at 1–5 keV are used to sputter the target, with a depth resolution of 5 nm. Sequential AES analysis at each depth reveals important information for the in-depth elemental distribution.

Owing to the high surface sensitivity of the technique, surface contamination is a major problem that may lead to important artifacts. Thus, analysis should be limited to clean surfaces. The UHV required for AES does not allow analysis of samples with high vapor pressure owing to outgassing inside the analysis chamber, which may affect both the vacuum and the surface chemistry of the material. The surface specificity of the technique is incompatible with the application of surface conductive coatings, to avoid electrostatic charging effects, that would enable the analysis of insulators. For analysis of nonconductive specimens, charge neutralization techniques are employed (*i.e.*, electron flood guns or grazing-angle electron incidence) to compensate for any shifting in the kinetic energy of Auger electrons that might otherwise induce artifacts. Possible electron beam artifacts related to poor thermal conductivity should be taken into account, such as the effects of surface modification and surface decomposition. Other important artifacts, such as differential sputtering, ion beam mixing, and cone formation may arise during ion sputtering studies and confuse the data for depth profiling. These effects are more frequent in the analysis of films more than 1 μm thick. AES is an excellent tool for the study of surface contamination of biomaterials, with additional applications for corrosion, wear, and tribology, by comparison of surface AES spectra with subsurface spectra obtained from depth profiling. AES, however, is considered destructive to organic materials, and care should be taken when analyzing soft tissue-biomaterial interfaces. Most AES applications on biomaterials have been performed on reference and retrieved implant surfaces.

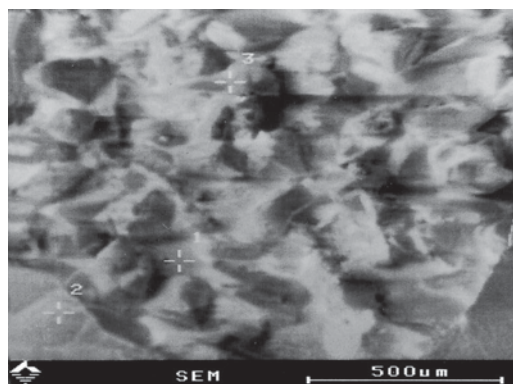


Fig. 3.7 a

Fig. 3.7 Auger electron spectroscopic analysis of an intact alumina bracket base (scale bar length = 500 μm). (a) Secondary electron image. (b) AES spectrum taken at point 3. (c) KLL image for C. (d) KLL image for O. Note the carbon contamination of the bracket base

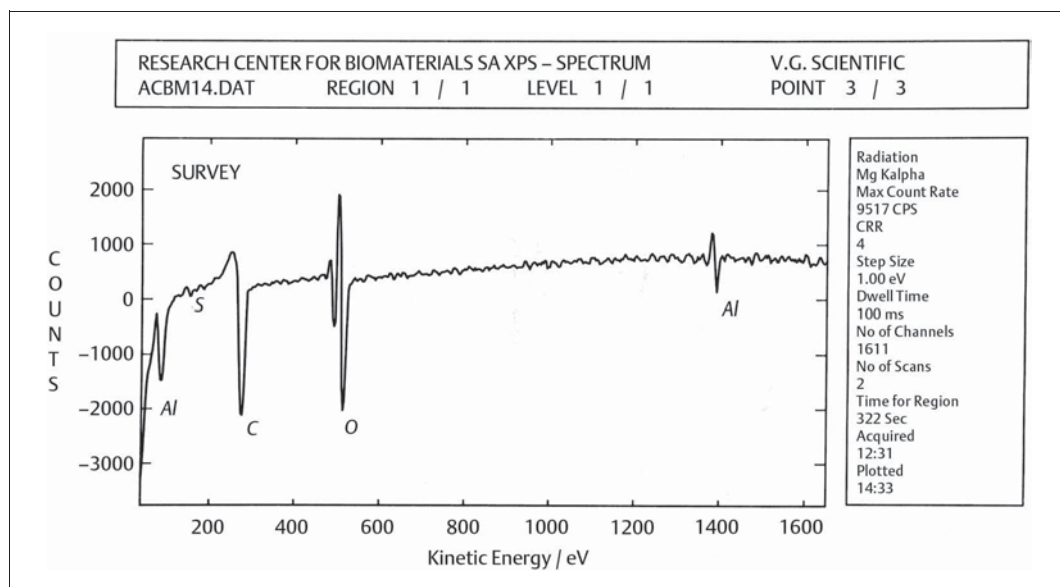


Fig. 3.7 b



Fig. 3.7 c

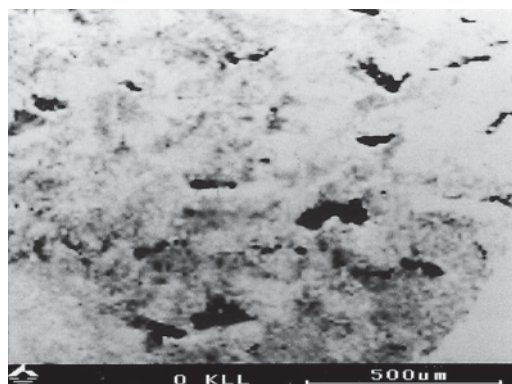


Fig. 3.7 d

Scanning Auger Microprobe (SAM)

Use of the scanning Auger microprobe (SAM) is the surface analysis analogue of EPMA. A microfocused electron beam at 3–30 keV is used to eject Auger electrons from the target with a lateral resolution of 30–200 nm. Imaging of the region is performed by secondary or back-scattered electrons, while the modes of SAM analysis include spot analysis, line scan analysis, and elemental mapping as in EPMA. Additionally, ion-induced depth profiling studies can be performed as in AES. The very high spatial resolution capacity of SAM is critical for the study of grain-boundary chemistry in metals, such as embrittlement, intragranular corrosion, corrosion cracking, and intergranular contamination. SAM is a highly effective method for studies involving solid-solid interactions like alloys, bonded or mechanically interlocked in-

terfaces, interfacial interactions, modification of frictional surfaces, and interaction of lubricants. SAM is a powerful method for the study of fracture surfaces. However, fracture of specimens should be performed inside the UHV chamber or usually in a preparative UHV chamber connected in series with the analysis chamber. This avoids environmental contamination, which occurs rapidly on reactive fracture surfaces and alters the chemical composition of the probed region owing to oxidation or adsorption of hydrocarbons. SAM is much more destructive to organic materials than is AES because of the relatively high electron beam voltages required. SAM has been used in the study of dental metal-ceramic interfaces, implant-tissue interfaces, and implant surfaces.

X-ray Photoelectron Spectroscopy (XPS)

In X-ray photoelectron spectroscopy (XPS) a core electron is ejected from a sample upon irradiation with X-rays of known energy. The photoemitted electrons are characterized by a binding energy, the difference between the total energies of the initial and final states, which is energy-resolved under UHV. The measured photoelectron intensities are plotted as a function of the binding energies. Upon relaxation of the atom, characteristic X-rays or Auger electrons are produced. Since electron analyzers are used in XPS and AES, the XPS spectrum contains Auger peaks as well. Usually Mg, Al or combined Mg/Al sources are used to produce photoelectrons having energies of 5–15 keV. Dual anodes are very useful for the analysis of samples emitting photoelectrons and Auger electrons of the same energy. In such cases resolution is enhanced by changing the incident X-ray energy, which affects only the kinetic energy of the photoemitted electrons. When high-resolution analysis is required, monochromatic X-ray sources should be used.

XPS is essentially a surface analysis technique with a depth of analysis ranging from 2 to 10 nm for photoelectrons with binding energies of 0–1100 eV and, as with other surface-specific techniques, requires UHV. The lateral

resolution in XPS may reach 50 μm for small-area analysis mode. XPS detects all elements except helium and can be applied nondestructively to organic materials, as shown in Figure 3.8a. The most important advantage of XPS is the ability to resolve shifts in the binding energy of the inner-shell electrons when the energy status of the valence electrons is changed, owing to alternations in the chemical environment that modify the nuclear attractive force for inner-shell electrons. Thus XPS can provide information about bonding state, oxidation state, change in crystal structure, and formation of new compounds. Identification of the chemical state is usually performed by peak deconvolution algorithms and assignment to reference spectra, as illustrated in Figure 3.8b. Quantitative analysis can be performed either by the use of standards or by obtaining elemental sensitivity factors. Typical accuracy in quantitative determinations is $\pm 10\%$.

Depth profiling analysis can be performed, as in AES, by nondestructive angle-resolved analysis or by ion sputtering. When the latter is used, the uncertainties related to the limitations of sputtering should be taken into account. Since XPS is very sensitive to chemical

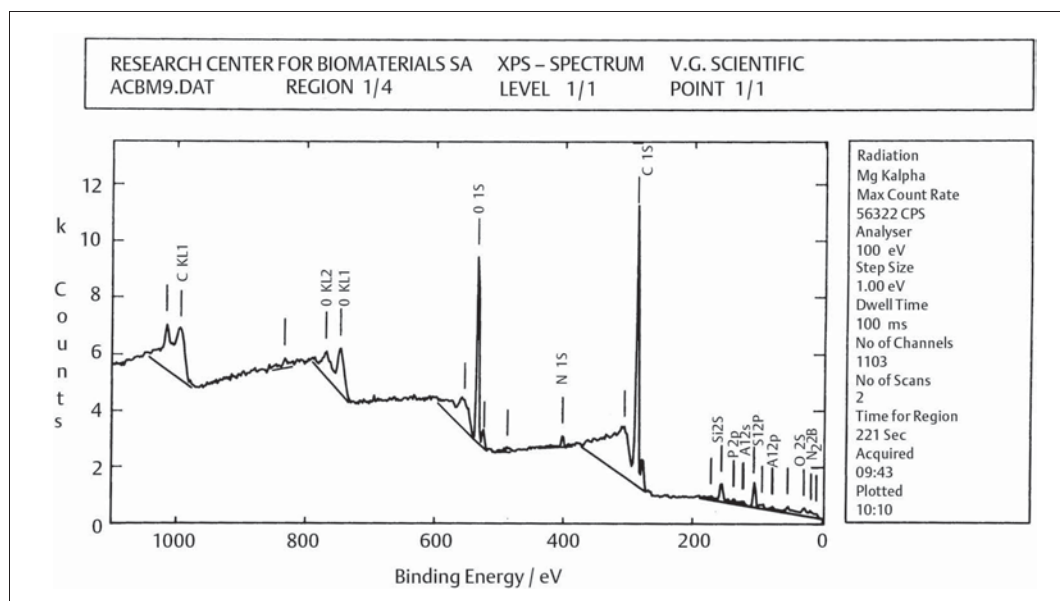


Fig. 3.8a

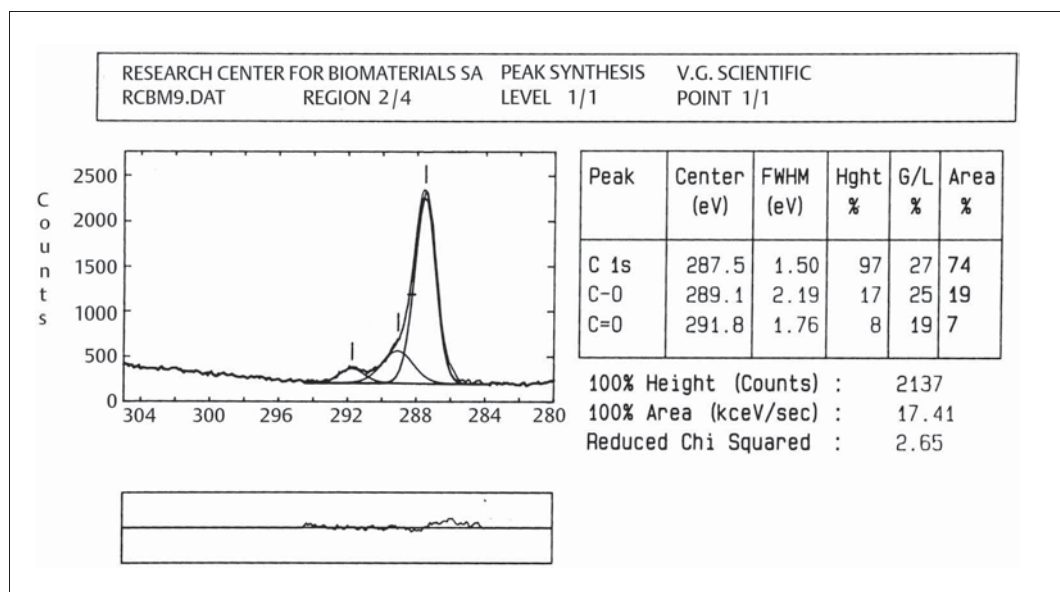


Fig. 3.8b

Fig. 3.8 Small-area X-ray photoelectron spectroscopic analysis of a visible-light cured, resin-modified glass-ionomer orthodontic adhesive. (a) Survey XPS spectrum of the directly irradiated surface. (b) Curve fitting of the C1s peak reveals three binding states: aliphatic, alcohol, and ester

shifting effects, the possibility of volume changes during sputtering is very high. XPS, as AES, requires no conductive coating. Analysis on insulators is thus associated with charging defects. However, charging is much lower than in AES, is always positive, and may be neutralized by electron flood guns. In some systems elemental or binding state imaging is feasible for elemental or molecular mapping purposes with a lateral resolution of 10–20 μm . In these systems complementary electron flood guns are used for imaging the analysis area through the analyzer, a procedure similar to secondary electron imaging in AES. Degassing of materials that are volatile under vacuum is important in XPS analysis and should be avoided. Surface

contamination, mostly of organic origin, should be removed by distilled solvents or mild ion sputtering before analysis. Since XPS can be used on organic materials, care should be taken to avoid vacuum-induced interactions such as polymerization and polycondensation. The nature of XPS precludes any application to hydrated specimens without the use of cryogenic stages. Nevertheless, XPS is the only surface analysis technique by which a structure-biocompatibility relationship has been established for several polymeric biomaterials. XPS has been used extensively in the study of biomaterial surfaces, such as of implants, amalgams, prosthodontic alloys, polymers, and adhesives.

Secondary Ion Mass Spectrometry (SIMS)

In secondary ion mass spectrometry (SIMS) primary ions from some source are focused on a sample surface and sputter surface atoms, molecules and ions; the latter are called secondary ions. These species are extracted from the sample surface by an electric field, and the positive or negative ions are mass-analyzed in a spectrometer. The data can be presented in terms of the ion distribution as a function of mass (spectrum), depth (depth profiling), and surface location (imaging). Both static and dynamic modes of SIMS can be employed. In static SIMS a very low sputtering rate is used, and a full-range spectrum is recorded with a sampling depth of a monolayer or more (2–5 nm). In dynamic SIMS the intensity of selected peaks in the mass spectrum is continuously recorded at a high sputtering rate as a function of depth to provide an in-depth elemental distribution profile for an uppermost region several micrometers in thickness. Dynamic SIMS is necessarily a destructive technique.

The sources used in SIMS are either duoplasmatron (O_2^+ and Ar^+ for mass scans and depth profiling), surface ionization (Cs^+) or liquid metal (Ga^+ for imaging). Neutral fast-atom bombardment may be used as well to minimize electrostatic charging, beam damage, and ionic migration when analyzing organic insulators. The energy of incident ions on the target is in the range 2–20 keV, and a 45°–90° angle of

incidence is employed, which are appropriate conditions for momentum transfer of the incident ions to the target atoms. The secondary ion yield produced depends on the incident ion energy, the angle of incidence, the target composition, the binding energy of the atoms, and particularly the ionization probability. The secondary ions produced from the target are subjected to energy filtering and then are mass-analyzed by quadrupole, magnetic sector, or time-of-flight spectrometers (in the order of increasing sensitivity). Charge neutralization is required for nonconductive samples. Two main designs are used in SIMS instruments: ion microprobes and ion microscopes for direct imaging. Ion microprobes are mostly used for quantitative depth profiling and less for surface analysis. Ion microscopes generate a secondary ion beam that can be used for direct imaging of the analyzed region. Ion microprobes offer superior spatial resolution (~ 20 nm). Both instrument types provide ionic and molecular imaging capacity (Fig 3.9).

SIMS detects all elements, including hydrogen, with high sensitivity (ppm to ppb). However, variation in detection sensitivity occurs for different elements on the same substrate and for the same element in different substrates. UHV is required in most applications. Quantification is difficult and requires ion-implanted standards. Quantification of molecular species is much more difficult than that of

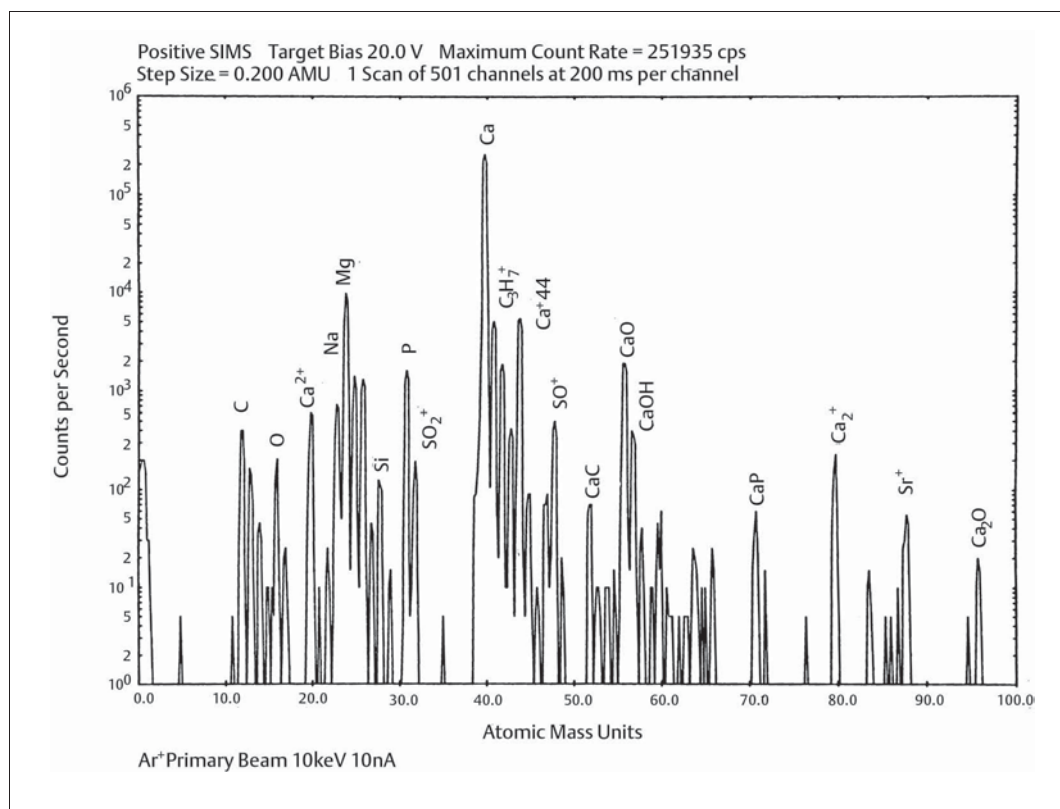


Fig. 3.9a

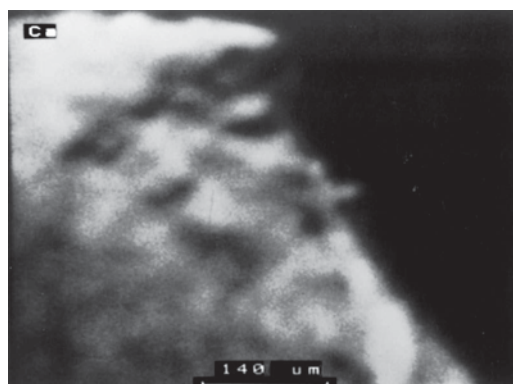


Fig. 3.9b

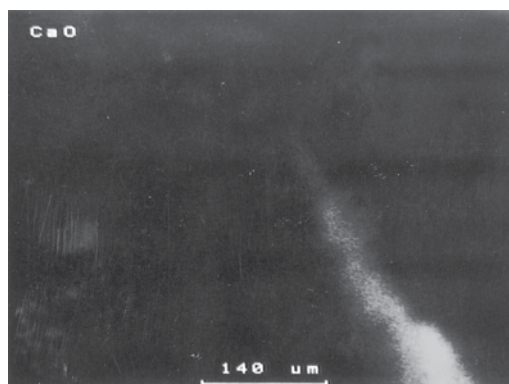


Fig. 3.9c

Fig. 3.9 Static secondary ion mass spectrometric analysis of a dentin surface treated with a self-etching primer (cross-sectional view: scale bar length = 140 μm). (a) Static SIMS spectrum. (b) Elemental imaging of Ca. (c) Molecular imaging of CaO

atomic species. SIMS is generally used for solving specific problems for specimens with known stoichiometry and matrix structure rather than for the chemical analysis of unknown samples, since the interpretation of spectra can be difficult. The nature of secondary electron emission in SIMS sets several limitations. Intermixing and recoiling target elements, beam-induced diffusion and migration of solute species, differential sputtering for multi-component systems, and depth-profiling artifacts like ion beam-induced roughness and crater edge-effects may complicate signal processing.

SIMS has been used successfully for the study of biomineralization in teeth and bone, using concentration profile analysis and molecular and ionic imaging. SIMS seems to be the only surface analysis technique available today that can detect trace elements at very high sensitivity (ppm to ppb) and high spatial resolution (μm to nm). Some of the most important SIMS applications deal with implant-tissue interactions and the remineralization potential of fluoride-containing solutions or dentifrices.

Fourier Transform Infrared Spectroscopy (FTIR)

When a sample is irradiated by infrared radiation (IR) at photon energies from about 0.05–0.5 eV, the molecules are excited into high vibrational states, owing to resonant absorption at frequencies characteristic of the chemical bonds present. Thus, information about the structures of organic and inorganic materials can be obtained. However, this is possible only when changes in dipole moment occur after irradiation. The principle of molecular characterization is that a given functional group vibrates at almost the same frequency, independently of the molecular environment, except in cases of coupling between different chemical groups, which results in frequency shifting. Plotting absorbance or transmittance against frequency yields the IR spectrum. Most studies are performed at the mid-IR region of $4000 - 400 \text{ cm}^{-1}$. (The wavenumber [unit cm^{-1}], which is the reciprocal of the IR wavelength, is usually plotted.) Originally, only dispersive instruments were available, in which the IR radiation was separated into different wavenumber components by the aid of gratings or prisms. With the advent of computerized Fourier transform infrared (FTIR) spectrometers, laser interferometers are used to modulate each IR frequency. Important advantages are offered, such as (a) high energy output, (b) simultaneous measurement of all frequencies at a very fast rate and reproducible frequency scale (which permits co-addition of spectra and thus a very high increase in signal-to-noise ratio), and (c) the ability to employ digital subtraction techniques for comparison

of spectra. These advantages have made possible the analysis of aqueous solutions previously not amenable to IR, owing to the strong water absorption and the performance of low-energy experiments for characterizing a variety of solid samples with enormous versatility.

A mid-IR-range FTIR spectrometer consists of a high-temperature cooled ceramic source, a potassium bromide splitter, an interferometer to modulate the intensity at each wavelength, and a He-Ne laser for continuous spectral calibration at 632.8 nm. The detector is either deuterated triglycine sulfate (DTGS) operating at room temperature or mercury cadmium telluride (MCT), which requires liquid-nitrogen cooling and is used selectively in low-energy experiments.

Apart from traditional transmission techniques used for gas, liquid, and powder analyses, new techniques have been introduced for non-destructive characterization of solid samples. FTIR is also employed as a detector in combined techniques such as gas chromatography and thermogravimetric analysis. The nondestructive FTIR characterization of solid surfaces or of solid-liquid interfaces has found increasing application in biomaterials research. The main techniques for surface analysis in FTIR spectroscopy are specular reflectance, internal reflectance, and photoacoustic and surface microscopies.

In specular reflectance spectroscopy the beam is reflected from a front surface of a sample at an angle equal to the angle of incidence. The reflected energy is small and depends upon

the angle of incidence and the refractive index, surface roughness, and absorption characteristics of the sample. The absorption bands may appear inverted or derivatized owing to the influence of the refractive index of the sample or the dielectric absorbance, and thus spectral data should be corrected by mathematical transformations (e.g., Kramers-Kronig), which produce transmission-like spectra. This external reflection technique is rarely used for the study of biomaterials because of sample smoothness and high reflectivity requirements and complications from diffuse reflectance interferences.

Another type of external reflectance method is reflection-absorption FTIR spectroscopy, in which the beam travels through a thin sample placed on a noninteracting reflective surface. The beam bounces off the reflective surface and passes again through the sample, producing data analogous to those obtained with the transmission technique. At incidence angles of $10^\circ - 60^\circ$, samples with film thickness of $0.5 - 20 \mu\text{m}$ can be analyzed. For thinner films grazing-angle analysis should be performed (angles of $60^\circ - 85^\circ$). The use of linear polarizers further improves sensitivity, since only the molecules with a dipole moment parallel to the plane of the incident and reflected beams absorb radiation, and has been shown effective in analyzing monolayers at a nanometer level. Polarization modulation experiments are used for the analysis of adsorbed monolayers by comparing the spectra obtained with the IR radiation polarized perpendicular (p-polarization) or parallel (s-polarization) to the sample surface. This method is useful for the analysis of thin coatings, adhesives, and lubricants.

In internal reflectance spectroscopy the sample is placed in contact against an IR-transparent crystal of high refractive index. The IR beam is focused onto the crystal edge and, if the angle of incidence is greater than the critical angle, the beam is totally internally reflected. At each reflection point an evanescent wave is generated that penetrates into the sample a short distance ($0.5 - 3 \mu\text{m}$, dependent on the wavelength of the radiation) and is attenuated at frequencies characteristic of the absorbing groups. As the intensity of the evanescent wave decays exponentially with the distance from the crystal surface, the technique is insensitive to sample thickness. The resulting spec-

trum resembles that for transmission, except that the bands at longer wavelengths are more intense because longer wavelengths penetrate deeper into the sample. According to the number of internal reflections, the systems available are characterized as attenuated total reflectance (ATR) when a single reflection occurs or multiple internal reflection (MIR) where multiple reflections are performed (Fig. 3.10). ATR is useful for strongly absorbing materials. Both types of accessories can be used for microsampling purposes when equipped with minicrystals.

A variety of internal reflection elements can be used in internal reflectance spectroscopy such as KRS-5 (ThI-ThBr, $n = 2.4$), ZnSe ($n = 2.4$), ZnS ($n = 2.2$), CdTe ($n = 2.6$), Si ($n = 3.5$) and Ge ($n = 4.0$), where n is the refractive index. One of the most popular crystals is KRS-5. This crystal has a spectral window comparable to that for transmission methods; it does not cleave upon pressure and is ductile, which is an advantage in establishing good contact with specimens. The depth of analysis is dependent on the wavelength of the radiation, the refractive index ratio between the sample and the crystal, and the angle of incidence. Non destructive angle-resolved depth profiling is possible by continuously varying the angle of incidence, provided that the critical angle is not exceeded. However, it should be mentioned that the contribution of the sample component near an interface to the overall spectrum is higher, regardless of the depth of beam penetration. Reproducible contact is required for comparison of spectra or for subtraction techniques.

A unique advantage of internal reflectance spectroscopy is the ability to study solid-liquid interfaces, especially in an aqueous environment. Flow cells, skin analyzers, and micro-ATR fiber optic probes have greatly expanded the technique for the study of biomaterial-biofluid interactions, the kinetics of protein absorption and protein conformation changes, and skin analysis *in vivo*.

One of the most common and important problems in internal reflectance spectroscopy is the selection of an inappropriate background reflectance spectrum. A clean, dry internal reflectance crystal placed in the cell position should be the reference. If the crystal is removed from the holder of the cell, a new back-

ground reference should be recorded. Cleaning of the crystal sampling surface should be performed between samples if there is a possibility of cross-contamination. For small samples microcells should be used to increase the contact area relative to the crystal surface area. In cases of incomplete crystal coverage, the sample should be positioned at the first reflection points where the IR beam is strongest and gives the best spectral quality.

In photoacoustic spectroscopy (PAS) the solid sample is placed in a sealed cell that is filled with an IR-transparent gas. Usually high-purity helium is preferred because of its high thermal conductivity, which results in the highest sensitivity. Upon irradiation, the fraction absorbed by the sample is transformed into heat, which propagates to the sample surface. It is transmitted to the gas and generates modulated pressure waves that are detected by a microphone or a piezoelectric device. The acoustic signal is passed to the spectrometer, referenced to a totally absorbing material like carbon black,

and recorded as an absorbance-type spectrum. PAS is suitable for analysis of highly absorbing materials. The depth of penetration into a sample depends on the thermal conductivity and heat capacity of the sample, and typically varies between 10 and 100 μm . Deeper sample areas are probed at low frequencies. Nondestructive depth profiling can be performed by changing the FTIR mirror velocity. The slower the mirror velocity, the greater the depth of penetration. The depth fractions may vary from 0.2 to 10 μm or more. Nevertheless, care should be taken at low mirror velocities to avoid photoacoustic saturation, which occurs when the IR radiation is absorbed within a length smaller than the thermal diffusion path of the sample. The main advantage of PAS is the minimal requirement for sample preparation. There is no need for contact with refractive crystals, and there are no geometric shape and roughness limitations. Rough surfaces possessing high surface-to-volume ratio increase PAS signal intensity. However, internal reflection

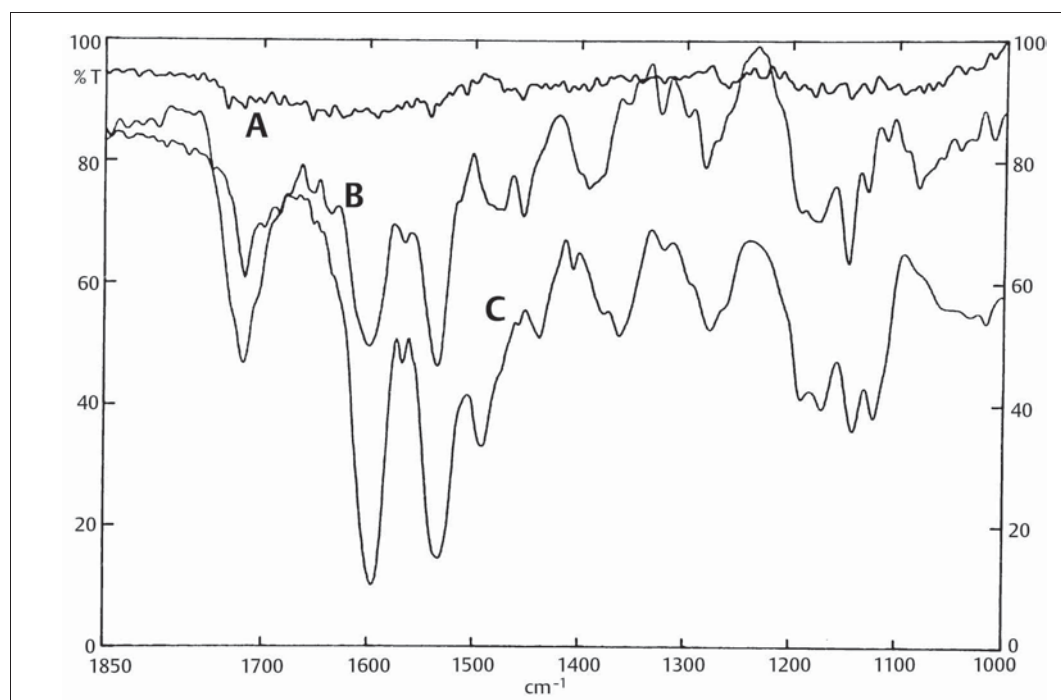


Fig. 3.10 Micro-multiple internal reflectance FTIR spectroscopic analysis of the effect of a primer used to mediate bonding of resin orthodontic adhesives on noble metal prosthodontic alloys: **A** original alloy surface spectrum; **B** alloy surface spectrum after primer treatment; **C** original primer. Note the changes in the relative intensity of the peaks in **B** relative to **C**, which imply molecular orientation effects due to secondary bonding

techniques yield higher-quality spectra than PAS. An important limitation of PAS is that degassing samples cannot be analyzed. This excludes moist or hydrated samples from the range of PAS applications.

In surface FTIR microscopy, grazing angle and internal reflectance cassegrainian objectives are attached to FTIR microscopes for surface analysis. A hemispherical microcrystal is used in internal reflectance objectives. The sample is observed under reflected light; the region of interest is isolated; the crystal is brought into contact with the sample surface, and finally the spectrum is recorded. The depth of analysis may vary between 0.2 and 2.0 μm , depending on the type of crystal used, and the lateral resolution may reach 30 μm . With grazing angle objectives, films less than 5 nm thickness may be analyzed, which may correspond to less than 1 ng. The introduction of FTIR imaging techniques has greatly expanded the analytical applications of FTIR microscopy. Molecular mapping (two-dimensional, three-dimensional, and cross-sectional analysis) and bond-ratio mapping capabilities provide important information for the molecular characterization of material surfaces and interfaces; the lateral resolution is much higher than for electron beam microanalysis techniques. The nondestructive nature, the ability to operate on hydrated specimens and the potential of applying complementary microscopic or micro-analytical techniques for multi-technique characterization have established FTIR microscopy as a popular microanalytical technique.

A major use of FTIR spectroscopy is in quantitative analysis. Matching of an unknown spectrum with a reference spectrum is the most positive form of identification. Otherwise, band-by-band assignments should be made,

based on reference databases or custom-built spectral libraries. Subtraction techniques can be employed for the interpretation of spectra, but care should be exercised in internal reflectance and photoacoustic spectroscopy, where the depth of beam penetration depends on the wavelength. Several techniques have been introduced for interpretation of spectra that are based upon mathematical algorithms that may assist quantitative analysis, such as factor analysis for determining the number of components in an array of mixtures or resolution-enhancement methods like derivative spectroscopy and peak deconvolution. Quantitative analysis is based upon Beer's law. Several techniques have been developed, such as the calibration curve method, the standard addition method, the absorbance ratio method, the internal standard method, and the coincidence band method. For quantitative analysis in internal reflectance spectroscopy it is essential that the sample is always in intimate contact with the same surface area of the crystal.

FTIR spectroscopy has been used extensively for the study of the degree of C = C conversion in dental dimethacrylate-based resins for various applications (sealants, adhesives, and restoratives) and the evaluation of the extent of the acid-base reaction in glass-ionomer materials and their modifications. Moreover, the effects of various conditioners and primers on the molecular composition of dentin have been investigated *in situ* by FTIR microsampling techniques. Another field dominated by FTIR spectroscopy is the characterization of the integuments formed on various dental materials *in vivo*. In most of these applications, internal reflection FTIR techniques are employed, either alone or in combination with complementary methods of instrumental analysis.

Raman Microspectroscopy

In Raman microspectroscopy, radiation from a monochromatic source, such as a laser, is focused on a sample microregion. The fraction of radiation scattered by the sample consists of a component of the exciting radiation known as the Rayleigh line and other weak lines called Raman lines. The frequency shifts of the Raman lines from the Rayleigh line correspond to the molecular vibrational frequencies within the

sample molecules. The plot of the Raman frequencies as a function of their intensities yields the Raman spectrum, which provides important information on the structure, orientation, and chemical state of a sample, provided that the vibrations alter sample polarizability. Raman spectra in most cases are complementary to IR.

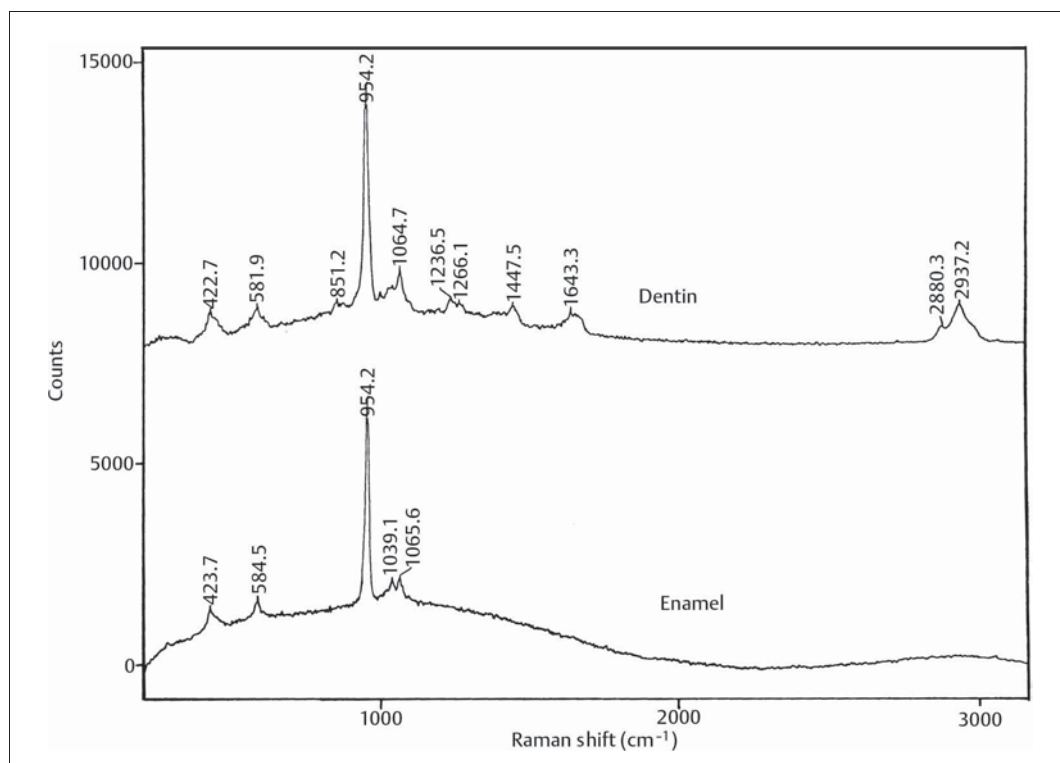


Fig. 3.11 Raman microspectroscopy of enamel and dentin surfaces. Note the characteristic shifts of dentin due to the presence of the organic phase

In Raman microspectroscopy the sample is viewed through a conventional optical microscope under bright-field or dark-field illumination. Analysis can be either in a spot mode with high spatial resolution or in a molecular imaging mode. For the latter, the molecular components of a sample are determined through their characteristic vibrational frequencies, and their distribution is mapped across the sample surface (molecular mapping). In some systems, confocal arrangement of the objective lens with stigmatic spectrometers and detectors is feasible for nondestructive in-depth analysis.

Raman microspectroscopy offers several advantages. The entire vibrational spectrum is probed with one instrument at increased sensitivity and at high spatial resolution ($\sim 1 \mu\text{m}$). Sampling is easily performed and is nondestructive for most applications. Raman microspectroscopy is much more sensitive to inorganic materials than is IR, especially for metal oxide systems. Raman spectra of solids and

crystals contain contributions from lattice vibrations at low frequencies that provide important information on crystal structure. Water demonstrates weak Raman scattering, and thus it is an ideal solvent. This explains the extensive use of the technique in studying aqueous solutions and biological fluids. Raman microspectroscopy can be a powerful tool for characterization of polymers, especially for components present in only 5–10% concentration. However, the main problem in such applications is the laser-induced fluorescence. The development of lasers emitting in the near-IR regions (e.g., neodymium-yttrium-aluminum garnet or Nd:YAG, $\lambda = 1.064 \mu\text{m}$) has greatly reduced fluorescence interferences, and their use is preferred for the analysis of polymers and samples of biological origin. Selection of the proper excitation laser is of major importance in Raman microspectroscopy. Dark-colored samples cannot be analyzed with the Nd:YAG laser owing to intense

background emission, and problems are encountered in the analysis of aqueous samples that absorb both the exciting laser radiation and the Raman-scattered fraction.

Another important parameter for the analysis of biological tissues or sensitive polymers is the laser power output. Typical laser powers used in Raman microspectroscopy vary from several milliwatts to several watts (W). How-

ever, focusing the laser beam results in power densities of several W/cm^2 to $10^3 \text{ W}/\text{cm}^2$ at the site being analyzed, which may overheat or burn the target, especially when prolonged spectral acquisition periods are used.

Figure 3.11 illustrates the application of Raman microspectroscopy to enamel and dentin. The organic phase in dentin causes a characteristic shift of the observed peaks.

Multi-technique Characterization

Many applications require the use of complementary analytical techniques for combined structural, elemental, and molecular characterization. Several commercial UHV systems offer options for multi-technique analyses like XPS/SIMS, AES/XRS, and SAM/EDS-EPMA in the same chamber. This eliminates surface contamination that can occur from intermediate exposure of the specimen to atmospheric conditions when the individual techniques are employed consecutively. An important factor to be considered for obtaining meaningful results is performing the analysis in a sequence of increasing damage potential (e.g., in the order of XPS, AES, SAM, and SIMS). The use of sputtering techni-

ques for depth-profiling analysis should be limited when XPS is used as part of the multi-technique characterization. This is very important for the analysis of organic materials, because graphite residues are left at the site where the beam hits the sample, as a result of the decomposition of the substrate. When combining nondestructive environmental techniques with UHV techniques, the latter should be applied after environmental analysis.

Although multi-technique characterization offers the ultimate analytical potential, it should be applied carefully to avoid artifacts of the previously discussed sequential analytical methods.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a highly important member of the general class of thermal analysis methods that includes thermomechanical analysis (dilatometry), thermogravimetric analysis, and differential thermal analysis. Differential scanning calorimetry is employed extensively to characterize industrial polymers and over the past decade has been increasingly used for study of orthodontic materials, particularly nickel-titanium archwire alloys (Chapter 4) and polyurethane elastomers (Chapter 8).

In conventional DSC two small pans, one containing the material to be analyzed and the other containing an inert reference material such as indium (or remaining empty), are heating at the same rate, typically 5°C or 10°C per minute (termed the ramp rate or scanning rate). The difference in thermal energy (power) sup-

plied to each pan to maintain equal heating rates is plotted as a function of temperature over the scanning range to yield the DSC curve or thermogram. The changes in the thermal power difference for the two pans are related to changes in the heat capacity (specific heat, c_p) of the material under study.

A schematic DSC plot for a polymeric material undergoing typical structural transformations is shown in Figure 3.12. The glass transition, at which the polymer transforms from a relatively rigid state to a flexible state (Chapter 1), causes a sigmoid on the DSC curve owing to the differences in heat capacity for the two states. The glass transition temperature (T_g) is conventionally designated as the point of inflection (midpoint of the glass transition range), where the sense of the curvature changes on the sigmoid. The subsequent formation of

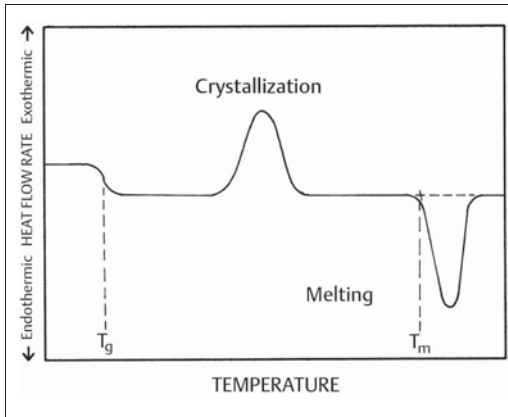


Fig. 3.12 Schematic DSC plot for a polymeric material undergoing a glass transition and subsequent crystallization, followed by eventual melting (From Rosen, 1993)

crystallites in the polymer microstructure releases thermal energy, so that this crystallization process appears as an exothermic peak on the DSC plot. Thermal energy is required

for eventual melting of the polymer, which appears as an endothermic peak. Figure 3.12 shows that the onset temperature (obtained by extrapolation of the baseline) is conventionally designated as T_m , since melting during the DSC analysis occurs at higher temperatures than the equilibrium melting point because of the dynamic heating conditions.

With the aid of computer software associated with the DSC apparatus, the areas (enthalpy values, ΔH) of the peaks on the DSC plots are readily obtained, along with the temperatures for any glass transition, crystallization, melting, or other structural transformation processes. Experiments can include subambient temperatures in the scanning range with the use of dry ice (to attain about -60°C) or liquid nitrogen (to attain about -150°C), the latter requiring a generally available special cooling accessory. Nitrogen is used as a purge gas in the DSC cell and provides heat transfer to the specimen. Other advantages of differential scanning calorimetry are that the experiments can be performed rapidly with the usual scanning

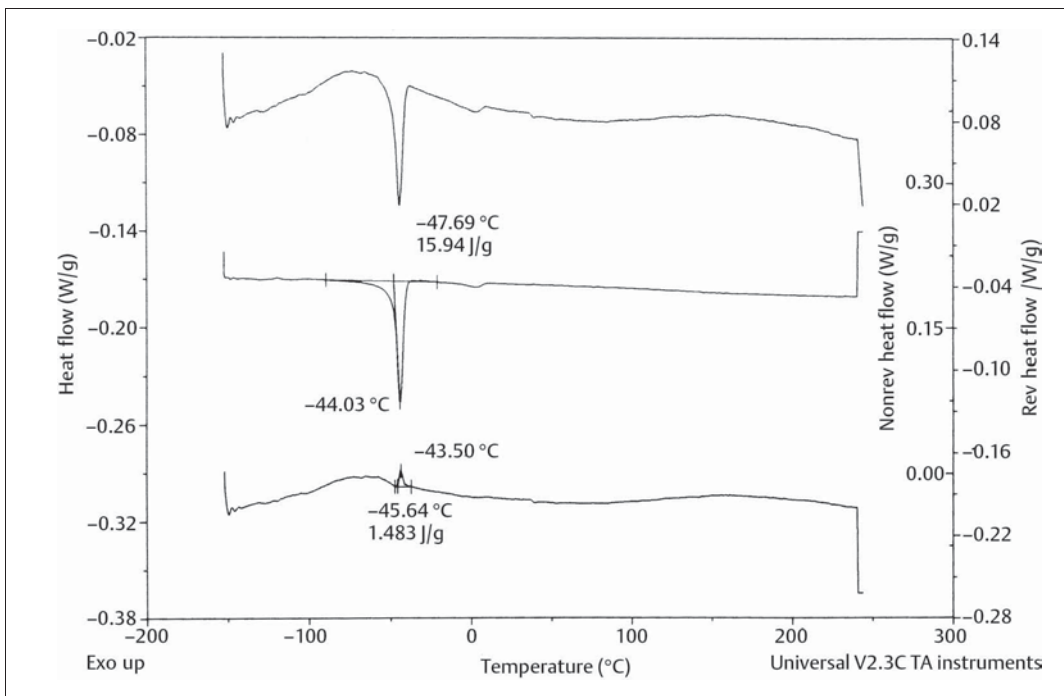


Fig. 3.13 TMDSC plot for Examix-Light Body silicone impression material (GC America, Alsip, IL, USA). The total (top), reversing (center), and nonreversing (bottom) heat flow curves are shown. The total heat flow curve would be obtained with conventional DSC

rates and temperature ranges, the specimen sizes are quite small (typically much less than 50 mg), and the analyses provide information about the bulk material, in contrast to X-ray diffraction.

Differential scanning calorimetry is particularly useful for studying phase transformations in the nickel-titanium archwire alloys, where there is substantial supporting engineering materials science literature about the DSC peaks for the NiTi phases. Several DSC plots for the nickel-titanium orthodontic alloys are discussed in Chapter 4. DSC has been employed to investigate the structural transformations occurring in polyurethane elastomers. As discussed in Chapter 8, inferences may be possible about the relative mechanical properties of different products, based upon the values of the glass transition temperatures.

While no articles have yet been published on its application to orthodontic materials, the recently developed technique of temperature-modulated differential scanning calorimetry (TMDSC) has provided new insight into

polymeric transformations in elastomeric maxillofacial and impression materials. The TMDSC procedure superimposes a small sinusoidal temperature waveform on the linear heating profile for standard DSC. Figure 3.13 presents the TMDSC curves for a silicone impression material, where the linear heating rate was 2 °C per minute and the sinusoidal waveform had an amplitude of 0.318 °C and a period of 60 sec. With TMDSC the total heat flow to the specimen can be subdivided into the reversing and nonreversing components. The sigmoid for the very weak glass transition process (near -125 °C) and the strong endothermic peak for crystalline melting can be seen on both the total and reversing heat flow curves in Figure 3.13, while the irreversible crystallization process is evident as an exothermic peak on the non-reversing heat flow curve. TMDSC is useful for separating phase transformations according to whether they have reversible or irreversible character and can provide insight into some transformations that would not be possible with conventional DSC.

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X-ray Fluorescence and Electron Probe Microanalysis

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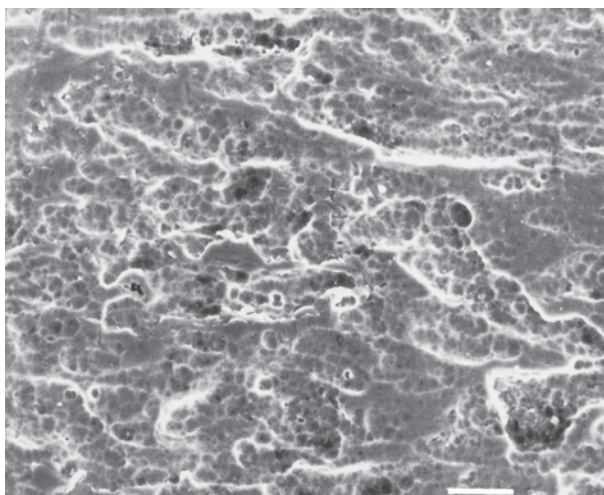
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4 Orthodontic Wires

William A. Brantley



SEM photomicrograph of the surface of as-received Nitinol SE wire

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Introduction

Desirable Properties for Orthodontic Wires

Orthodontic wires, which generate the bio-mechanical forces communicated through brackets for tooth movement, are central to the practice of the profession. In the rational selection of wires for a particular treatment, the orthodontist should consider a variety of factors, including the amount of force delivery that is desired, the elastic (working) range or springback, formability or ease of manipulation, and the need for soldering or welding to assemble an appliance. *In vivo* corrosion, with release of metal ions, and the ensuing biocompatibility concerns for the patient are also important factors that will be discussed in Chapters 14 and 15.

Currently, orthodontists principally use wires of four major base metal alloy types: stainless steel, cobalt-chromium-nickel, nickel-titanium and β -titanium (Table 4.1). With the need to maintain a relatively large inven-

tory, orthodontists must be concerned with the costs of the wires, which can vary considerably among wire alloys as well as among the companies that distribute these products. For example, selection of the more expensive nickel-titanium archwires can be somewhat offset by the reduction in the number of wire changes required during patient treatment.

Manufacturing of Orthodontic Wires

The starting point for the manufacturing of orthodontic wires is the casting of an ingot having the appropriate alloy composition. This ingot is then subjected to a series of mechanical reduction operations until the cross section is sufficiently small for wire drawing. The drawing for a round wire must be performed in a series of steps until the final desired diameter is achieved, since the alloy rapidly work-hardens during each step of this process. Generally,

Table 4.1 Compositions and mechanical properties of the four major orthodontic wire alloy types

Wire Alloy	Composition (wt%)	Modulus of Elasticity (GPa)	Yield Strength (MPa) ^a	Springback ^b
Austenitic stainless steel	17–20 % Cr, 8–12 % Ni, 0.15 % C (max), balance mainly Fe	160–180	1100–1500	0.0060–0.0094 (AR) 0.0065–0.0099 (HT)
Cobalt-chromium-nickel (Elgiloy Blue)	40 % Co, 20 % Cr, 15 % Ni, 15.8 % Fe, 7 % Mo, 2 % Mn, 0.15 % C, 0.04 % Be	160–190	830–1,000	0.0045–0.0065 (AR) 0.0054–0.0074 (HT)
β -titanium (TMA)	77.8 % Ti, 11.3 % Mo, 6.6 % Zr, 4.3 % Sn	62–69	690–970	0.0094–0.011
Nickel-titanium	55 % Ni, 45 % Ti (approx. and may contain small amounts of Cu or other elements)	34	210–410	0.0058–0.016

From Brantley, 1997.

^aThe values of yield strength correspond to 0.1 % permanent tensile strain. ^bThe terms AR and HT for the stainless steel and Elgiloy Blue alloys refer to the as-received and heat-treated conditions, respectively.

more than one company is involved in the complex wire manufacturing sequence.

Wires with a rectangular cross section are manufactured from round wires, using a Turk's head apparatus having two pairs of rollers positioned at right angles. Accordingly, orthodontic wires with rectangular or square cross-sections have some inevitable rounding at the corners. This can make an important contribution to the archwire-bracket torque delivery, particularly when there is relatively tight engagement of the wires in the bracket slots.

Heat treatments are necessary during wire manufacturing to eliminate the extensive work hardening that occurs during the various

stages of mechanical reduction. Information about these heat treatments is proprietary to the manufacturers, as are details about the reduction per pass, the number of passes, and the die and die lubrication materials. Special atmospheric conditions are needed for manufacturing the titanium-containing orthodontic wires because of the reactivity of these alloys with air. There is a tendency for the titanium-containing alloys to bind to the die or roller surfaces, resulting in increased surface roughness compared to other wire alloys. This can significantly affect the archwire-bracket friction, as will be discussed later.

Wire Alloys

Gold Alloy Wires

Historically, gold alloy wires were first used in orthodontic practice, although these noble metal wires have minimal use currently because of their much greater cost compared to the popular base metal wires. The gold alloy wire compositions were generally similar to those of the type IV gold casting alloys, and their modulus of elasticity was approximately 100 GPa. Thus, the gold alloy wires had elastic force delivery much less than that for stainless steel wires with the same cross-sectional dimensions and segment lengths (Table 4.1). Substantial hardening and strengthening of these gold alloy wires could be achieved by an appropriate heat treatment, which resulted in the same ordering phase transformation that can be used to provide hardening and strengthening for the types III and IV gold casting alloys.

Stainless Steel Wires

By the 1950s stainless steel alloys were used for most orthodontic wires. Stainless steel wires remain popular because of their favorable combination of low cost and excellent formability, along with good mechanical properties. These wires can be soldered and welded for the fabrication of complex appliances, although it is necessary to use solder to provide reinforcement to the weld joints.

The stainless steel alloys used for orthodontic wires are of the “18-8” austenitic type, containing approximately 18% chromium and 8% nickel (Table 4.1). While a report several decades ago showed that a 17-7 precipitation-hardenable stainless steel alloy had higher yield strength and greater resilience in bending than the commonly used stainless steel wire alloys, this alloy never achieved commercial popularity for orthodontic wires.

The chromium in the stainless steel forms a thin, adherent passivating oxide layer that provides corrosion resistance by blocking the diffusion of oxygen to the underlying bulk alloy. Approximately 12–13 wt% chromium is required to impart the necessary corrosion resistance to these alloys. The chromium, carbon, and nickel atoms (and atoms of other metals in the composition) are incorporated into the solid solution formed by the iron atoms. Since the nickel atoms are not strongly bonded to form some intermetallic compound, the likelihood of *in vivo* slow nickel ion release from the alloy surface is increased, which may have implications for the biocompatibility of these alloys.

Typically, stainless steel orthodontic wires are fabricated from AISI (American Iron and Steel Institute) types 302 and 304 alloys. Research using X-ray diffraction has shown that austenitic stainless steel orthodontic wires may not always possess the single-phase austenitic structure that is based upon a face-cen-

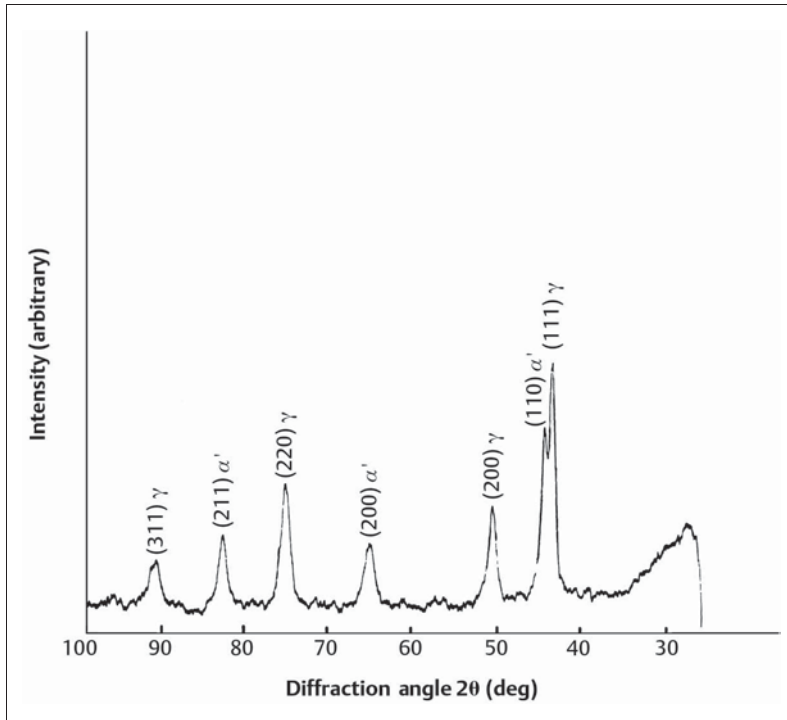


Fig. 4.1 X-ray diffraction pattern from 0.017 in $\times$ 0.025 in (0.43 mm $\times$ 0.64 mm) as-received TruChrome stainless steel wire (Rocky Mountain Orthodontics, Denver, CO, USA), showing a duplex structure of austenitic (γ) and martensitic (α') phases. (Adapted from Khier *et al*, 1988)

tered cubic (fcc) arrangement of the iron atoms. A two-phase structure was found for some as-received stainless steel wires (Fig. 4.1), where the austenitic (γ) phase was accompanied by a body-centered cubic (bcc) martensitic (α') phase. Other as-received wires had the single-phase austenitic structure (Fig. 4.2). The X-ray diffraction patterns from these wires show the preferred crystallographic orientation that would be expected for wrought alloys. No peaks were evident from the $(\text{CrFe})_4\text{C}$ phase, expected to be present in these alloys.

Formation of the martensitic phase results in a substantial reduction in the modulus of elasticity, from about 200 GPa for fully annealed stainless steel alloys to about 150 GPa for heavily cold-worked alloys. Extensive cold working can increase the yield strength of these austenitic stainless steels from about 275 to over 1100 MPa. The foregoing range for modulus of elasticity in tension has been measured for stainless steel orthodontic wires of varying sizes, and indicates the variations in the levels of final cold-working mechanical deformation found in the as-manufactured wires. Heat treatment of some duplex-structure

wires at three different temperatures of approximately 400 °C, 500 °C and 600 °C eliminated the α' phase (Fig. 4.3), but other heat-treated wires maintained the two-phase structure found in as-received wires. There was little difference in the effects of the heat-treatment temperature on the X-ray diffraction patterns, and the wrought microstructure of the as-received wires was maintained after heat treatment at the highest temperature of 600 °C. The difference in the heat-treatment behavior was hypothesized to arise from variations in the carbon content of the wire alloys.

Heat treatment of stainless steel wires at temperatures between 400 °C and 500 °C is recommended to eliminate some residual stresses resulting from wire manufacturing and to prevent premature breakage of complex appliances during assembly. Heat treatment of straight as-received wire segments yielded changes in the modulus of elasticity (E) in tension ranging from minimal to an increase of about 10% and increases in yield strength (YS) from less than 10% to more than 40%, depending upon the wire size. The modulus of resilience, which represents the total elastic

Fig. 4.2 X-ray diffraction pattern from 0.050 inch (1.27 mm) diameter as-received Tru-Chrome stainless steel wire, showing a single-phase austenitic (γ) structure. (Adapted from Khier *et al*, 1988)

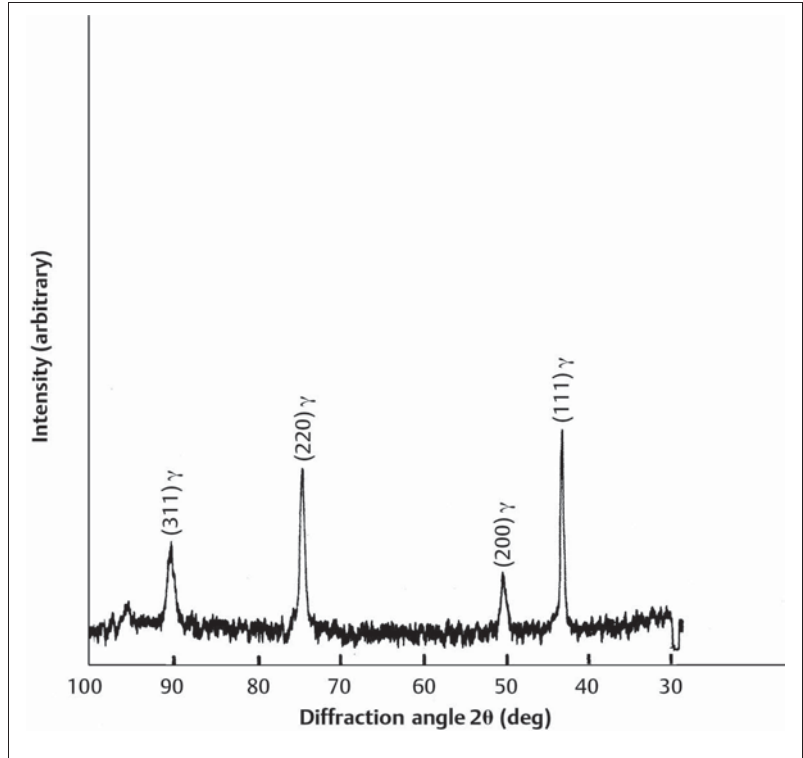
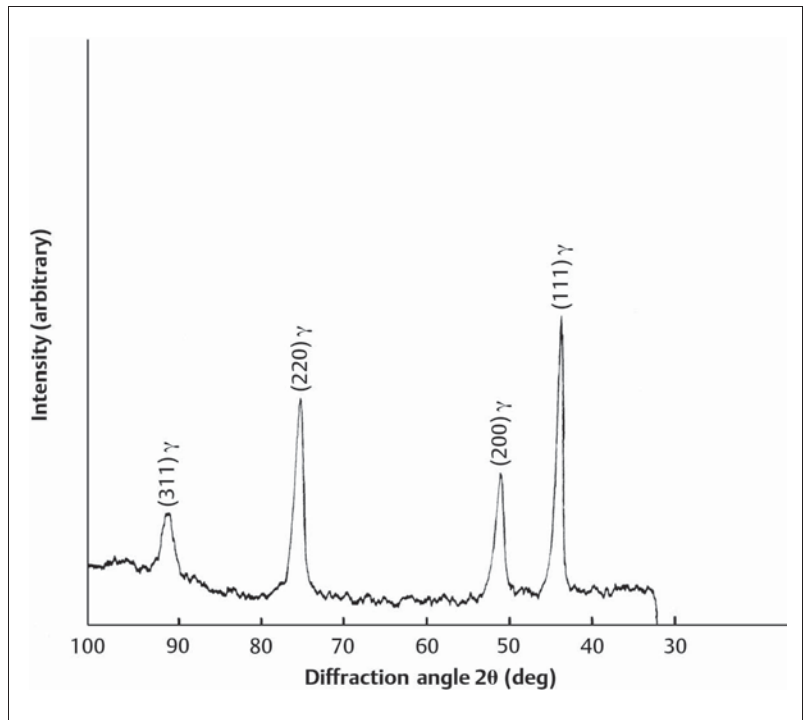


Fig. 4.3 X-ray diffraction pattern from 0.017 in $\times$ 0.025 in (0.43 mm $\times$ 0.64 mm) Tru-Chrome stainless steel wire after heat treatment at 480°C, showing a single-phase austenitic (γ) structure. (Adapted from Khier *et al*, 1988)



biomechanical energy or spring energy in the wire, is given approximately by $(YS)^2/2E$. This expression can be used to estimate the changes in elastic spring energy resulting from the heat treatment.

It was also found that substantial increases in the elastic limit occurred after heat treatment of simple closing loops fabricated from straight wire segments. From a clinical viewpoint, the major purpose of heat-treating stainless steel orthodontic appliances is to minimize breakage rather than to achieve significant increases in resilience.

Heat treatment of stainless steel orthodontic wires at temperatures above 650°C must be avoided because rapid recrystallization of the wrought structure takes place, with deleterious effects on the wire properties. Heating stainless steel to temperatures between about 400°C and 900°C causes reaction of the chromium and carbon to form chromium carbide precipitates at the grain boundaries. Loss of chromium from the iron solid solution matrix of stainless steel depletes the chromium content near the grain boundaries to below the 12–13 wt% level required for passivation. This sensitization can cause the stainless steel alloy to become susceptible to intergranular corrosion.

The free-handed soldering of stainless steel orthodontic appliances should be performed rapidly with a well-controlled torch and the use of a flux. The solder joint is primarily formed by surface wetting and mechanical retention of the solder at the workpiece surfaces. In contrast, electrical resistance or spot welding of stainless steel causes melting and solidification of the alloy, with localized loss of the wrought microstructure and increased stresses in the surrounding heat-affected zone where joint failure is most likely to occur.

Cobalt-Chromium-Nickel Wires

A cobalt-chromium-nickel orthodontic wire alloy (Elgiloy) was developed during the 1950s by the Elgiloy Corporation (Elgin, IL, USA). This alloy, which was originally used for watch springs, is available in four tempers (levels of resilience) that are color-coded by the manufacturer: blue (soft), yellow (ductile), green (semi-resilient), and red (resilient). Discussions with the manufacturer indicate that all four

alloy tempers have the same composition (Table 4.1); differences in mechanical properties arise from variations in the wire processing. As with the stainless steel alloys, the corrosion resistance of Elgiloy arises from a thin passivating chromium oxide layer on the wire surface.

The Elgiloy Blue alloy is very popular with many orthodontists because the as-received wire can easily be manipulated into desired shapes and then heat treated to achieve considerable increases in strength and resilience. This heat treatment can be performed easily with the aid of an electrical resistance welding apparatus, and the manufacturer provides a special paste that indicates when the appropriate conditions of temperature and time have been achieved. A furnace heat treatment for 10 minutes will achieve the same result.

It has been found that the maximum YS for straight, 0.41 mm diameter, wire segments is obtained with a heat-treatment temperature of about 500°C. Heat treatment of four different loop configurations (open, helical open, closed, and helical closed) at this temperature decreased their mean deflection/force characteristics (*i.e.*, increased the stiffness). This heat treatment causes complex precipitation processes that substantially increase the yield strength of the alloy.

Heat treatment of straight segments of Elgiloy Blue wires in several round and rectangular sizes yielded modest increases of about 10% in *E* and large increases of about 20–30% in YS. The other three tempers of Elgiloy have mechanical properties that are similar to tempers that are available with less expensive stainless steel wire alloys. These tempers, which are also responsive to heat treatment, are not as popular for orthodontics as the Elgiloy Blue wires.

Because of its “soft feel” (due to relatively low YS) during manipulation, orthodontists can mistakenly believe that as-received Elgiloy Blue wires have substantially lower elastic force delivery than stainless steel wires. In reality, the values of modulus of elasticity for the Elgiloy Blue and stainless steel orthodontic wires are very similar, as shown in Table 4.1. Other than the major differences in composition (Table 4.1), the stainless steel and Elgiloy Blue wire alloys have similar force delivery and joining characteristics. The Elgiloy Blue wires contain a comparable amount of nickel

to that found in the stainless steel wires, which may present concerns about biocompatibility to some orthodontists.

Another interesting clinical use of Elgiloy Blue wires is fabrication of the fixed lingual quad-helix appliance, which produces slow maxillary expansion for the treatment of maxillary constriction or crossbite in the primary and mixed dentitions. The force delivery from an 8 mm activation for appliances fabricated from stainless steel and Elgiloy Blue wires of 0.032, 0.036, and 0.038 in (0.81, 0.91, and 0.97 mm) diameters was found to vary significantly with appliance size and wire diameter but was independent of alloy type. This result would be anticipated from the very similar values for the modulus of elasticity of the two alloys (Table 4.1).

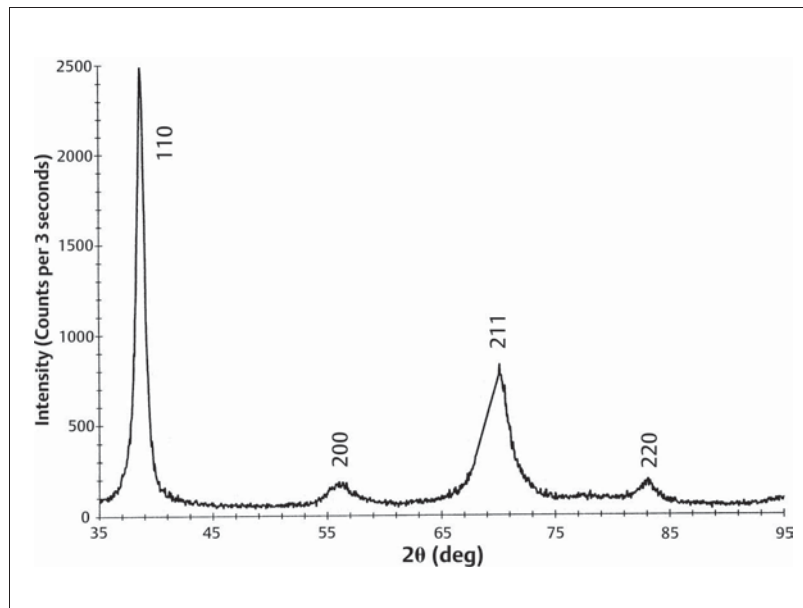
Beta-Titanium Wires

A β -titanium wire for orthodontics is marketed by the Ormco Corporation (Glendora, CA, USA). The commercial name for this wire is TMA, which represents “titanium-molybdenum alloy”. The β -titanium alloy was conceived for orthodontic use about two decades ago by Burstone and Goldberg, who recognized its potential for delivering lower biomechanical forces com-

pared to the stainless steel and cobalt-chromium-nickel alloys. Table 4.1 shows that the elastic modulus for the β -titanium wires is approximately 40% that of the stainless steel and Elgiloy Blue wires. Because of the much lower value of elastic modulus, despite lower values for yield strength, the β -titanium wires have significantly improved values of springback (YS/E), which markedly increase their working range for tooth movement.

A second clinical advantage of the β -titanium wires is excellent formability, which is due to their bcc structure. The addition of molybdenum to the alloy composition (Table 4.1) stabilizes the high-temperature bcc β -phase polymorphic form of titanium at room temperature, rather than the hexagonal close-packed α -phase. The X-ray diffraction pattern for a β -titanium (TMA) orthodontic wire in Figure 4.4 shows a single-phase bcc structure, with the broadened peaks and preferred crystallographic orientation expected for a heavily cold-worked alloy. The many slip systems available for dislocation movement in the bcc crystal structure account for the high ductility of the β -titanium wires. The zirconium and zinc in the alloy composition contribute increased strength and hardness, and their presence avoids the formation of an embrittling ω phase during wire processing at elevated tempera-

Fig. 4.4 X-ray diffraction pattern from 0.016 in $\times$ 0.022 in (0.41 mm $\times$ 0.56 mm) as-received β -titanium (TMA) wire. (An abstract describing this study is found in Brantley *et al*, J Dent Res, 1998)



tures. This wire processing can be problematic because of the reactivity of titanium, and there have been reports that some batches of TMA archwires are susceptible to fracture during clinical manipulation, despite the inherent excellent formability of the β -titanium alloy.

While heat treatment by the orthodontist is not recommended for the β -titanium wires, heat treatment of the alloy by the manufacturer between approximately 700°C and 730°C, followed by water quenching, yields a nearly all- β microstructure. Subsequent aging at approximately 480°C results in precipitation of the α -phase and a maximum value of springback for the TMA wires. Recent research has shown that a Ti-15V-3Cr-3Al-3Sn β -titanium wire may have improved formability and springback, but this new alloy does not appear to have had commercial application.

The third clinical advantage of β -titanium is that it is the only orthodontic wire alloy possessing true weldability. As previously noted, welded joints for stainless steel and Elgiloy Blue appliances require additional mechanical reinforcement with solder. Detailed optimum settings for welding β -titanium wires with the capacitance (single-pulse) and transformer (multiple-pulse) welding apparatuses available to the orthodontist have been published.

The β -titanium wires are generally the most expensive of the orthodontic wire alloys, but the greater cost is frequently considered by orthodontists to be offset by the combined advantages of intermediate force delivery (Table 4.1) and the excellent formability and weldability when fabrication of more complex appliances is required. With increased interest in the biocompatibility of orthodontic materials, another important feature of the β -titanium wires is their absence of nickel that is present in the other three major wire alloy types. The excellent corrosion resistance and biocompatibility of β -titanium is due to the presence of a thin, adherent, passivating surface layer of titanium oxide (TiO₂).

Scanning electron microscope (SEM) examination of β -titanium orthodontic wires has revealed relatively rough surfaces that are attributed to adherence or cold welding by the titanium to the dies or rollers during wire processing. This surface roughness contributes to the high values of archwire-bracket sliding friction measured in the laboratory, along with lo-

calized sites of cold welding or adherence by the wire to the bracket slots. A recently developed N⁺ ion implantation technique for β -titanium (Ormco) has markedly improved the measured values of *in vitro* sliding friction. The ion implantation yields high concentrations of nitrogen within a few tens of nanometers from the wire surface. Additional research is required to ascertain whether hard titanium nitride near-surface phases are formed during the ion implantation.

Nickel-Titanium Wires

The pioneer for the development of nickel-titanium wires for orthodontics was Andreasen, who published articles with colleagues advocating their use in the early 1970s. The first nickel-titanium orthodontic wire alloy (Nitinol) was marketed by the Unitek Corporation (now 3M Unitek, Monrovia, CA, USA). The generic name "nitinol" that is applicable to this group of nickel-titanium alloys originates from *nickel*, *titanium* and the Naval Ordnance Laboratory where the alloys were developed by Buehler and associates.

The Nitinol orthodontic wire offered a modulus of elasticity approximately 20 % that of the stainless steel wires, along with a very wide elastic working range. This was particularly evident when this wire was tested in cantilever bending with 12.5 mm segments, where the permanent set did not exceed 5° after bending 90° by the ADA specification test procedure.

Two new superelastic nickel-titanium wires, Chinese NiTi (marketed as Ni-Ti by Ormco) and Japanese NiTi (marketed as Sentalloy by GAC International, Islandia, NY, USA) were subsequently introduced during the mid-1980s. When clinically realistic 6 mm segments (corresponding to interbracket distances) of these wires were tested in cantilever bending, an extensive and nearly horizontal region (superelastic plateau) of constant bending moment was observed upon unloading (deactivation), as shown for the superelastic Ni-Ti alloy in Figure 4.5. (With the tension test, where there is uniform stress over the cross section, the loading and unloading superelastic plateaus are both horizontal.) These bending characteristics can be contrasted with those for the non-superelastic Titanal alloy (Lancer) in Figure 4.6.

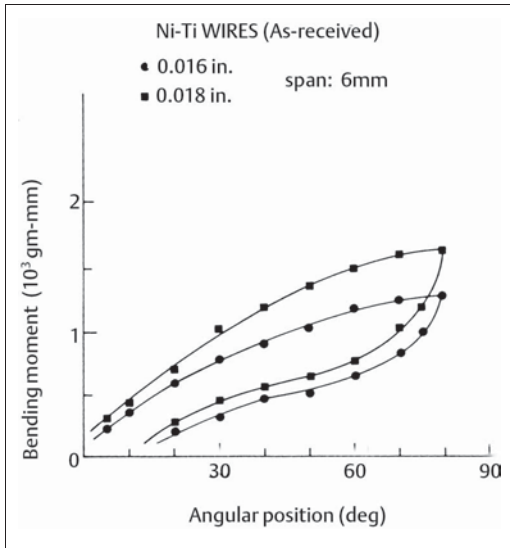


Fig. 4.5 Cantilever bending curves for two sizes of as-received Ni-Ti superelastic wires. (Adapted from Khier *et al*, 1991)

The springback (difference between the maximum deflection and the final deflection after deactivation) for as-received NiTi wires was found to be approximately 65° – 70° for three superelastic alloys and 40° – 60° for three non-superelastic alloys, respectively, with an original bending deflection of 80° .

Heat treatment of the Japanese NiTi wires at 500°C was found to significantly alter the superelastic force plateau that occurred during unloading of three-point bending test specimens. This behavior has been exploited by GAC International, who offers three levels of force delivery by the Sentalloy wires. It was also observed that heat treatment at 600°C eliminated the superelastic behavior. Subsequent experiments established that this heat treatment response at 500°C and 600°C occurred with other superelastic wire alloys (Fig. 4.7). The bending properties of nonsuperelastic nickel-titanium wires are not affected by heat treatments over the same 500°C to 600°C temperature range.

In the early 1990s a NiTi orthodontic wire alloy (Neo Sentalloy) with true shape memory at the temperature of the oral environment was introduced by GAC International. Many manufacturers now offer similar shape-memory NiTi

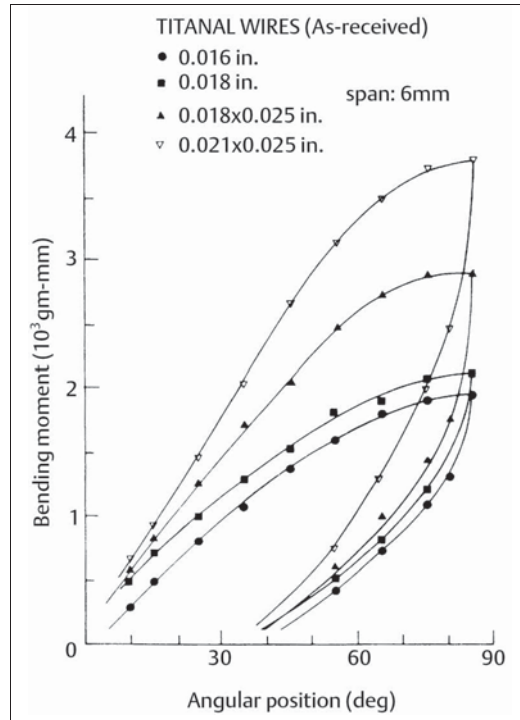


Fig. 4.6 Cantilever bending curves for four sizes of as-received Titanal nonsuperelastic wires. (Adapted from Khier *et al*, 1991)

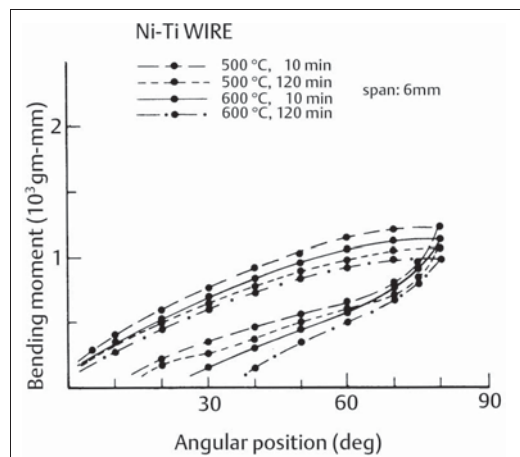


Fig. 4.7 Cantilever bending curves for 0.016 in (0.41 mm) diameter Ni-Ti wire after heat treatment at 500°C and 600°C for 10 minutes and 2 hours. (Adapted from Khier *et al*, 1991)

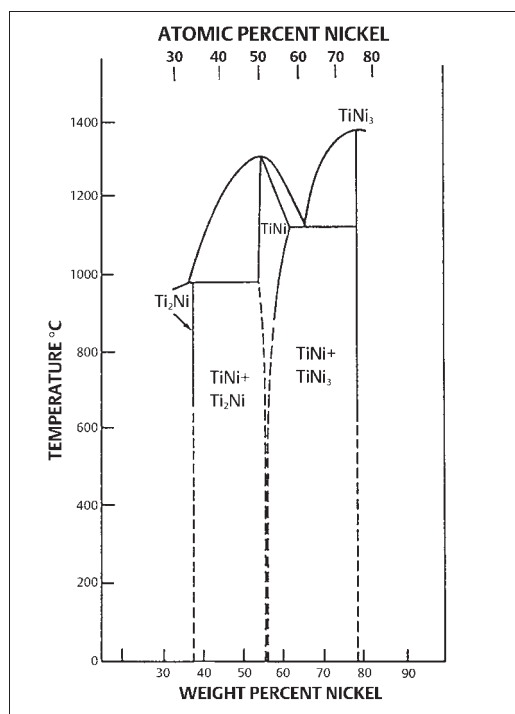


Fig. 4.8 Nickel-titanium binary phase diagram, showing the region near the intermetallic compound NiTi that is relevant for orthodontic wires. (From Goldstein *et al*, 1987)

orthodontic wires, which might be considered to have an optimum combination of light force delivery and springback under clinical conditions. However, this hypothesis needs to be verified by clinical studies, and the original Ni-

tinol wire remains popular. Some orthodontists have been concerned about biocompatibility of these wires because of their high nickel content.

The complex metallurgical nature of the nickel-titanium orthodontic wires and its relevance to clinical applications has spawned many research investigations that are the principal focus of the remainder of this chapter. The nickel-titanium wires contain approximately equiatomic proportions of nickel and titanium, and are based upon the intermetallic compound NiTi (sometimes written as TiNi). Examination of the binary phase diagram (Fig. 4.8) reveals that some deviation from stoichiometry is possible for NiTi. X-ray energy-dispersive spectroscopic (EDS) analyses with the SEM suggest that commercial orthodontic wires are generally titanium-rich. The results of a recent study are shown in Table 4.2. Particles with dimensions typically less than 1–2 μm and containing a large atomic fraction of titanium were found in the surfaces and cross sections of all wire samples examined. The small size of these particles prevented accurate determination of their compositions by EDS.

There are two major NiTi phases in the nickel-titanium wires. Austenitic NiTi (hereafter termed austenite) has an ordered bcc (CsCl-type) structure (sometimes termed B2), that occurs at high temperatures and low stresses. Martensitic NiTi (hereafter termed martensite) has been reported to have a distorted monoclinic, triclinic, or hexagonal structure, and forms at low temperatures and high stresses. The shape-memory effect (SME) is

Table 4.2 Surface and bulk compositions of several nickel-titanium wires

Wire Product	Surface Titanium Concentration (at%)	Bulk Titanium Concentration (at%)
BioForce (GAC)	50.5 $\pm$ 0.1	50.7 $\pm$ 0.4
Ni-Ti (Ormco)	49.9 $\pm$ 0.1	50.2 $\pm$ 0.2
Nitinol SE (3M Unitek)	50.0 $\pm$ 0.2	50.4 $\pm$ 0.2
Titanal XR (Lancer)	49.3 $\pm$ 0.2	50.2 $\pm$ 0.3
Nitinol (3M Unitek)	50.1 $\pm$ 0.2	51.2 $\pm$ 0.2
Nitinol XL (3M Unitek)	50.0 $\pm$ 0.3	50.6 $\pm$ 0.2

Abstracts describing these studies are found in Bradley *et al*, 1996 and Mitchell *et al*, 1996. Values are mean $\pm$ standard deviation ($n = 6$). Bulk titanium concentrations were obtained at two different depths on three cross-sectioned wire segments

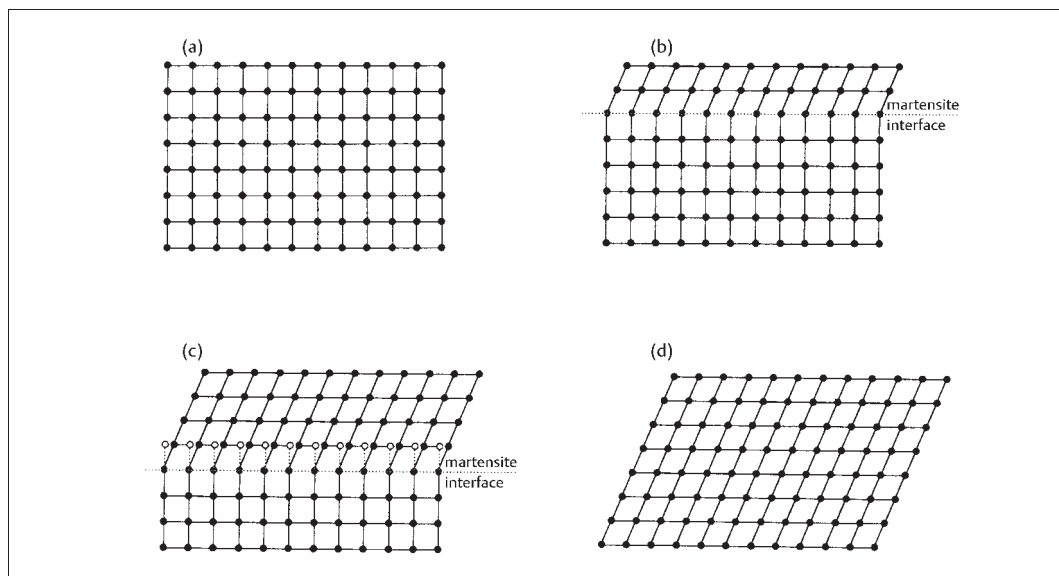


Fig. 4.9 Schematic illustration of twinning processes occurring in nickel-titanium alloys for the reversible transformation between austenitic and martensitic NiTi. (From Duerig *et al*, 1990)

associated with a reversible martensite $\leftrightarrow$ austenite transformation, which occurs rapidly by crystallographic twinning at the atomic level (Fig. 4.9). In some cases an intermediate R-phase having a rhombohedral crystal structure may form during this transformation process.

There are several important phase transformation temperatures for the nickel-titanium alloys. On cooling, the M_s (martensite-start) and M_f (martensite-finish) temperatures are the temperatures at which the transformation to martensite begins and is completed, respectively. Analogously, on heating, the A_s (austenite-start) and A_f (austenite-finish) temperatures are the temperatures at which the transformation to austenite begins and is completed, respectively. Similar transformation temperatures of R_s and R_f may be defined for the R-phase. The transformation temperature range (TTR) for each of the three structures (austenite, R-phase, and martensite) refers to the temperature range for the start and completion of the transformation to that particular structure. For the stress-induced formation of martensite, an additional M_d (martensite-deformation) temperature is defined as the highest temperature at which it is possible to have martensite. Above the M_d temperature the

stress to form martensite by twinning is greater than the stress for the irreversible movement of dislocations by slip.

Nitinol and other nonsuperelastic nickel-titanium orthodontic wire alloys contain substantial quantities of heavily cold-worked and stable martensite. The A_s temperatures for these alloys are much higher than room temperature and the temperature of the oral environment. The shape-memory wire alloys have A_f temperatures that are below the temperature of the oral environment, so that the wires have essentially the completely austenitic structure *in vivo*. The superelastic (but not true shape-memory) alloys have microstructures that are incompletely transformed to austenite at the temperature of the oral environment. The A_f temperatures for these wires can be much greater than 37 °C.

The foregoing differences in the phase transformation behavior for the three major types of nickel-titanium orthodontic wires can be clearly observed with differential scanning calorimetric (DSC) analyses. The DSC plots or thermograms are shown in Figure 4.10 for the superelastic alloy Nitinol SE, Figure 4.11 for the shape-memory alloy Neo Sentalloy, and Figure 4.12 for the nonsuperelastic alloy Nitinol.

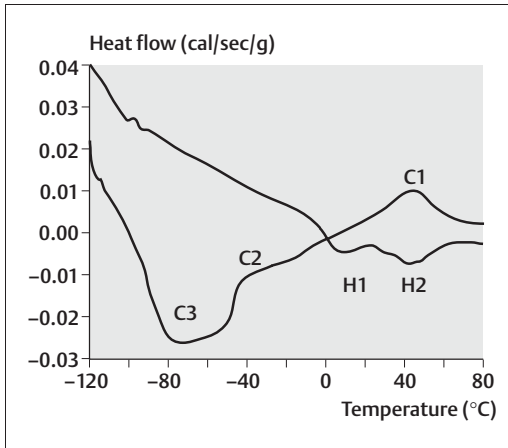


Fig. 4.10 DSC heating and cooling curves for Nitinol SE. (Adapted from Bradley *et al*, 1996)

For the superelastic alloy Nitinol SE in Figure 4.10, peak H1 on the heating DSC curve corresponds to the transformation from martensite to R-phase, and peak H2 corresponds to the transformation from R-phase to austenite. On cooling, peak C1 corresponds to the transformation from austenite to R-phase, and peak C2 corresponds to the transformation from R-phase to martensite. There is only a small amount of hysteresis (difference in TTR) for the forward and reverse transformations between R-phase and austenite (peaks H2 and C1), but considerable hysteresis occurs for the forward and reverse transformations between martensite and the R-phase (peaks H1 and C2). It can be seen that the A_f temperature on heating is about 60 °C, so that this alloy will be a mixture of R-phase and austenite at the temperature of the oral environment.

For the superelastic nickel-titanium alloy Ni-Ti, complete transformation to austenite occurs only slightly above the temperature of the oral environment, since the A_f temperature on heating is about 40 °C. Under *in vivo* conditions, this alloy is predominantly austenite with some R-phase. This alloy has heating and cooling DSC curves that are similar to Figure 4.10 and contain two peaks for the forward and reverse martensite $\leftrightarrow$ austenite transformations.

For the shape-memory alloy (Neo Sentalloy) in Figure 4.11, there is a single peak (H) on the heating DSC curve that corresponds to the di-

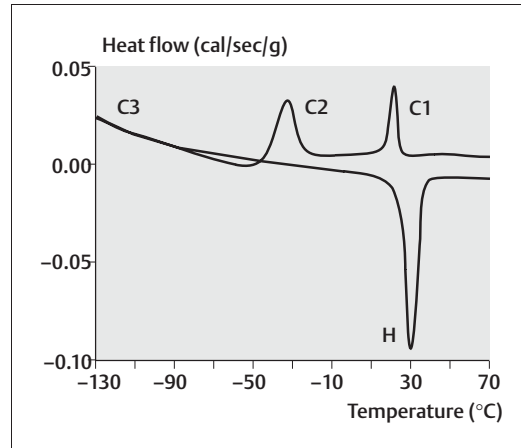


Fig. 4.11 DSC heating and cooling curves for Neo Sentalloy. (Adapted from Bradley *et al*, 1996)

rect transformation from martensite to austenite. There are two peaks on the cooling curve: peak C1 for the transformation from austenite to R-phase and peak C2 for the transformation from R-phase to martensite. There is again considerable hysteresis for the TTR in the forward and reverse directions for the complete transformation between the martensite and austenite. Figure 4.11 shows that Neo Sentalloy has essentially a completely austenitic structure at the temperature of the oral environment. Similar heating and cooling DSC curves were also observed for the shape-memory alloy Titanal LT (Lancer Orthodontics, Carlsbad, CA, USA).

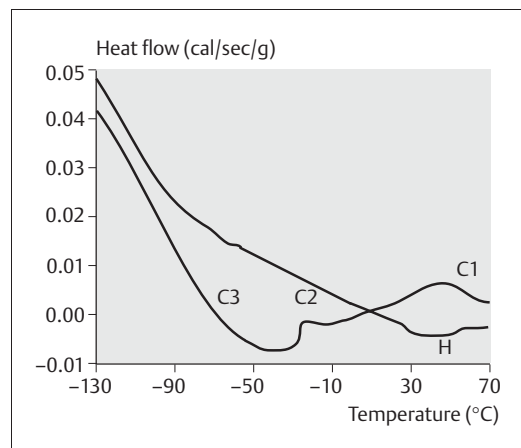


Fig. 4.12 DSC heating and cooling curves for Nitinol. (Adapted from Bradley *et al*, 1996)

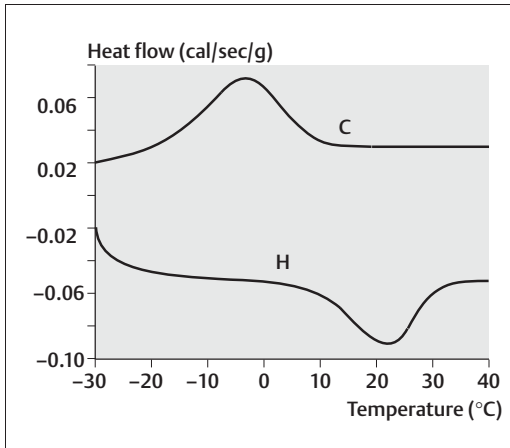


Fig. 4.13 DSC heating and cooling curves for 27°C Copper Ni-Ti. (From McCoy, MS thesis, 1996. An abstract describing this study is found in McCoy *et al*, 1997)

For the nonsuperelastic alloy Nitinol there is a weak and broad single peak (H) on the heating DSC curve in Figure 4.12 that corresponds to the direct transformation from martensite to austenite. The cooling curve contains two peaks: peak C1 for the transformation from austenite to R-phase and peak C2 for the transformation from R-phase to martensite. As in Figures 4.10 and 4.11, there is considerable hysteresis between the TTR on the heating and cooling curves for the overall transformation between the martensitic and austenitic phases. Figure 4.12 shows that this alloy is composed of martensite, austenite and perhaps R-phase at the temperature of the oral environment.

In their DSC study, Bradley *et al* found that an additional low temperature peak (designated as C3) appeared to occur on the cooling curve near the limit of resolution for the Ni-Ti superelastic alloy and the Titanal LT shape-memory alloy. Locations of possible C3 peaks for Nitinol SE (Fig. 4.10), Neo Sentalloy (Fig. 4.11), and Nitinol (Fig. 4.12) have been placed near the cooling curves, but these peaks cannot be resolved by DSC, if they exist. The C3 peak would represent an additional low-temperature phase transformation within the complex martensitic structure, and such low-temperature transformations have been reported by Chen *et al*, using electrical resistivity measurements.

In 1994 Ormco Corporation introduced a new orthodontic wire alloy, Copper Ni-Ti, which is available in three temperature variants of 27°C, 35°C, and 40°C, corresponding to the austenite-finish temperatures for the completion of the martensite-to-austenite transformation. Shape-memory behavior is reported by the manufacturer to occur for each variant at temperatures exceeding the specified temperature. These variants would be useful for different types of orthodontic patients. For example, the 27°C variant would be useful for mouth-breathers; the 35°C variant is activated at normal body temperature; and the 40°C variant would provide activation only after consuming hot food and beverages.

In a recent study the 27°C Copper Ni-Ti wire alloy contained a single peak on both the heating and cooling DSC curves (Fig. 4.13), indicating direct transformation from martensite to austenite on heating and from austenite to martensite on cooling, without an intermediate R-phase. In contrast, the 35°C Copper Ni-Ti and 40°C Copper Ni-Ti (Fig. 4.14) wire alloys exhibited two overlapping peaks on heating, corresponding to transformation from martensite to R-phase followed by transformation from R-phase to austenite. All three Copper Ni-Ti variants had a single peak on the cooling DSC curve, corresponding to direct transformation from austenite to martensite. The A_f tempera-

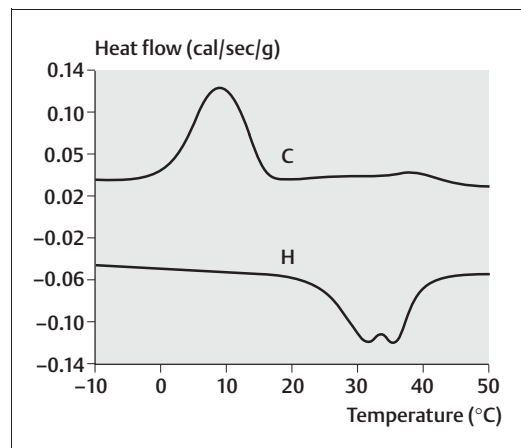


Fig. 4.14 DSC heating and cooling curves for 40°C Copper Ni-Ti. (From McCoy, MS thesis, 1996. An abstract describing this study is found in McCoy *et al*, 1997)

tures for the three variants were within 3 °C of the values reported by the manufacturer.

Mean enthalpy changes (ΔH) obtained by DSC for the forward and reverse martensite $\leftrightarrow$ austenite transformations are compared for the three Copper Ni-Ti variants, Neo Sentalloy and Nitinol in Table 4.3. It can be seen that the mean values of ΔH for the three Copper Ni-Ti variants are higher than that for Neo Sentalloy. The lowest mean enthalpy change for Nitinol is anticipated, since this wire alloy contains substantial quantities of stable work-hardened martensite. Table 4.3 also shows that the overall enthalpy change is different for the forward and reverse transformations. Figures 4.13 and 4.14 reveal that there is a large hysteresis between the forward and reverse transformations for the Copper Ni-Ti variants. The mean values of ΔH in Table 4.3 are comparable to those reported in other DSC studies of the nickel-titanium orthodontic wires. Values of ΔH from 3.6 to 5.7 cal/g have been reported in the materials science literature for cold-worked and heat-treated non-orthodontic nickel-titanium alloys.

Elemental analyses using SEM/EDS have indicated that the three Copper Ni-Ti variants have very similar compositions of approximately 44% nickel, 51% titanium, slightly less

than 5% copper, and 0.2–0.3% chromium (values in at%). Kusy has reported that Copper Ni-Ti contains nominally 5–6 wt% copper and 0.2–0.5 wt% chromium. The 27 °C variant contains 0.5% chromium to compensate for the effect of copper in raising the A_f temperature above that of the oral environment, and the 40 °C variant contains 0.2% chromium. However, the sensitivity available with the SEM/EDS apparatus did not permit detection of significant differences in the chromium contents of the three variants. The DSC results that R-phase can exist in the 35 °C and 40 °C Copper Ni-Ti variants over certain temperature ranges may not be inconsistent with previous reports that Cu-Ni-Ti alloys having more than approximately 5% copper do not contain the R-phase.

Kusy has suggested that the nickel-titanium orthodontic wire products can alternatively be classified into the following three categories, rather than the foregoing classifications of superelastic, nonsuperelastic and true shape memory:

- The martensitic-stabilized alloys do not possess shape memory or superelasticity, because the processing of the wire creates a stable martensitic structure. These are the nonsuperelastic wire alloys such as Nitinol.
- The martensitic-active alloys employ the thermoelastic effect to achieve shape memory; the oral environment raises the temperature of the deformed arch wire with the martensitic structure so that it transforms back to the austenitic structure and returns to the starting shape. This thermoelastic shape memory can be observed by the clinician if a deformed archwire segment is warmed in the hands. These are the shape-memory wire alloys such as Neo Sentalloy and Copper Ni-Ti.
- The austenitic-active alloys undergo a stress-induced martensitic (SIM) transformation when activated. These alloys display superelastic behavior (termed pseudoelastic in the materials science literature), which is the mechanical analogue of the thermoelastic shape-memory effect (SME). An austenitic-active alloy does not exhibit thermoelastic behavior when a deformed wire segment is warmed in the hands. These alloys are the superelastic wires that do not possess thermoelastic shape memory at the tem-

Table 4.3 Mean enthalpy changes (ΔH) and standard deviations (SD) obtained from heating and cooling DSC curves for some nickel-titanium wires

Wire Tested	ΔH (heating) cal/g	SD	ΔH (cooling) cal/g	SD
27 °C Copper Ni-Ti	2.71	0.16	3.50	0.58
35 °C Copper Ni-Ti	3.30	0.02	3.75	0.07
40 °C Copper Ni-Ti	3.71	0.13	4.60	0.15
Neo Sentalloy	1.68	0.18	0.89	0.07
Nitinol	0.93	–*	0.38	–

From McCoy, MS thesis (1996). An abstract describing this study is found in McCoy *et al*, 1997. Mean values and standard deviations (SD) for the enthalpy changes were obtained from three nominally identical samples ($N = 3$) of each Copper Ni-Ti variant and Neo Sentalloy, whereas only one sample of Nitinol* was evaluated by DSC

perature of the oral environment, such as Nitinol SE. Referring to Figure 4.5 for the cantilever bending deformation of Ni-Ti superelastic wires, the nearly horizontal region on the loading (activation) curve corresponds to stress-induced transformation of austenite in the as-received wires to martensite. The reverse transformation from martensite back to austenite takes place during unloading (deactivation).

X-ray diffraction (XRD) has been used extensively to study the phase relationships in the nickel-titanium orthodontic wires. The XRD patterns of as-received Ni-Ti, Titanal, Neo Sentalloy, and the 35°C and 40°C variants of Copper Ni-Ti at room temperature are shown in Figures 4.15 to 4.19. The XRD peaks in Figures 4.17 to 4.19 have been indexed using data from ICDD (International Center for Diffraction Data, Swarthmore, PA, USA) powder standards 18-899 for austenitic NiTi and 35-1281 for martensitic NiTi (Chapter 3).

These XRD patterns indicate that both Ni-Ti and Titanal contain a mixture of austenite and martensite at room temperature, with a higher proportion of martensite in Titanal. X-ray diffraction patterns similar to Figure 4.15 were found for two other superelastic wire alloys, and there were only minor differences for the round and rectangular sizes analyzed. Like-

wise, X-ray diffraction patterns similar to Figure 4.16 were found for two other nonsuperelastic wire alloys, and there were again only minor differences for round and rectangular sizes. In contrast, Neo Sentalloy is almost entirely austenite at room temperature (Figures 4.17), and a similar result has been found for the 27°C variant of Copper Ni-Ti. The amount of martensite increases on going to the 35°C and 40°C variants of Copper Ni-Ti (Figures 4.18 and 4.19), as expected from the increases in their A_f temperatures. There is substantial preferred crystallographic orientation for both the austenitic and martensitic phases in all of these alloys, when the relative intensity of the XRD peaks from the wire specimens are compared to those for the ICDD powder standards.

Heat treatments of the three superelastic alloys were performed at 500°C and 600°C for 10 minutes and 2 hours, followed by XRD analysis. It was found that the heat treatments at 500°C decreased the relative intensity of the martensite peaks (Fig. 4.20), which were essentially eliminated after heat treatment at 600°C (Fig. 4.21). This result meant that the M_s temperature was suppressed below room temperature by the heat treatment, so that very little of the austenite transformed back to martensite on cooling. Significant sharpening of the XRD peaks for the superelastic alloys after the

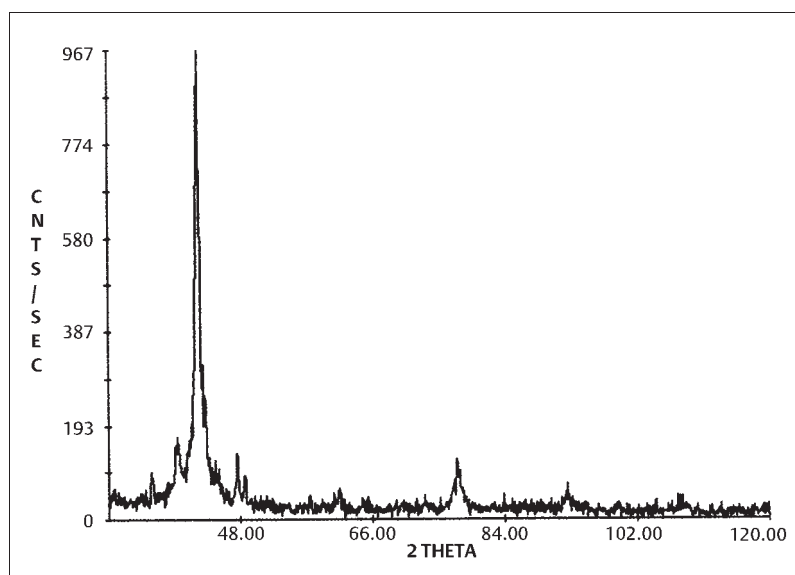


Fig. 4.15 XRD pattern for 0.016 in (0.41 mm) diameter as-received Ni-Ti. (From Khier, PhD dissertation, 1988)

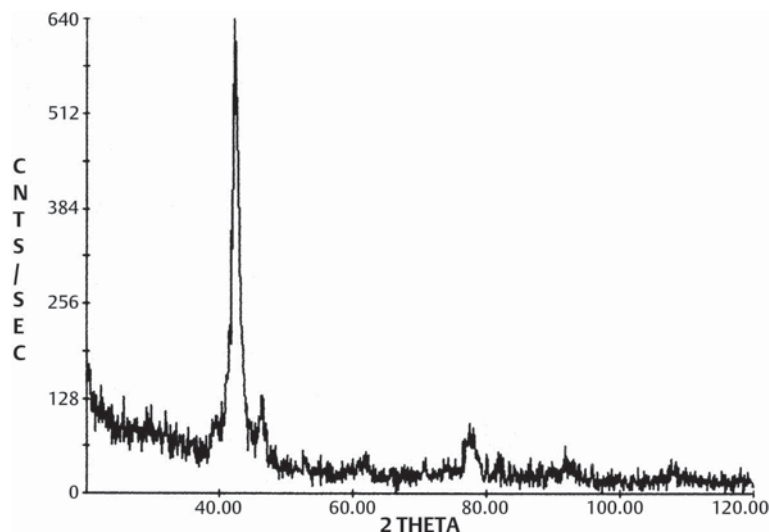


Fig. 4.16 XRD pattern for 0.016 in (0.41 mm) diameter as-received Titanal. (From Khier, PhD dissertation, 1988)

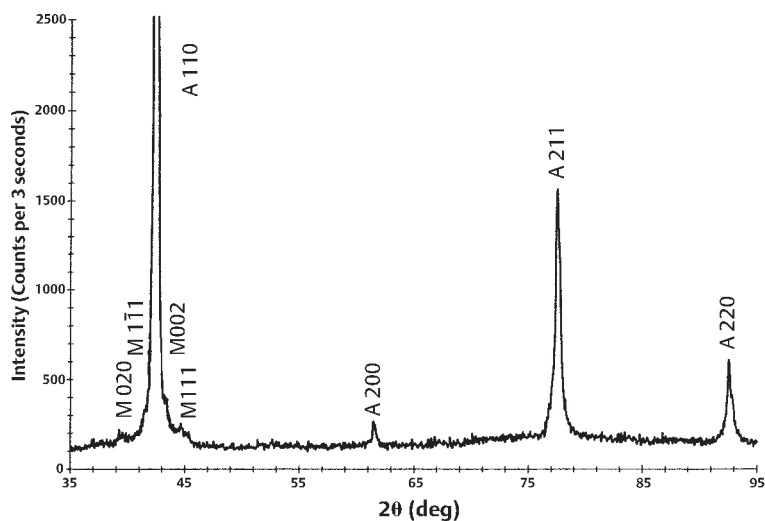


Fig. 4.17 XRD pattern for 0.016 in $\times$ 0.022 in (0.41 mm $\times$ 0.56 mm) Neo Sentalloy. (An abstract describing this study is found in Brantley *et al*, 1998)

Fig. 4.18 XRD pattern for 0.016 in $\times$ 0.022 in (0.41 mm $\times$ 0.56 mm) 35 °C Copper Ni-Ti. (An abstract describing this study is found in Brantley *et al*, 1998)

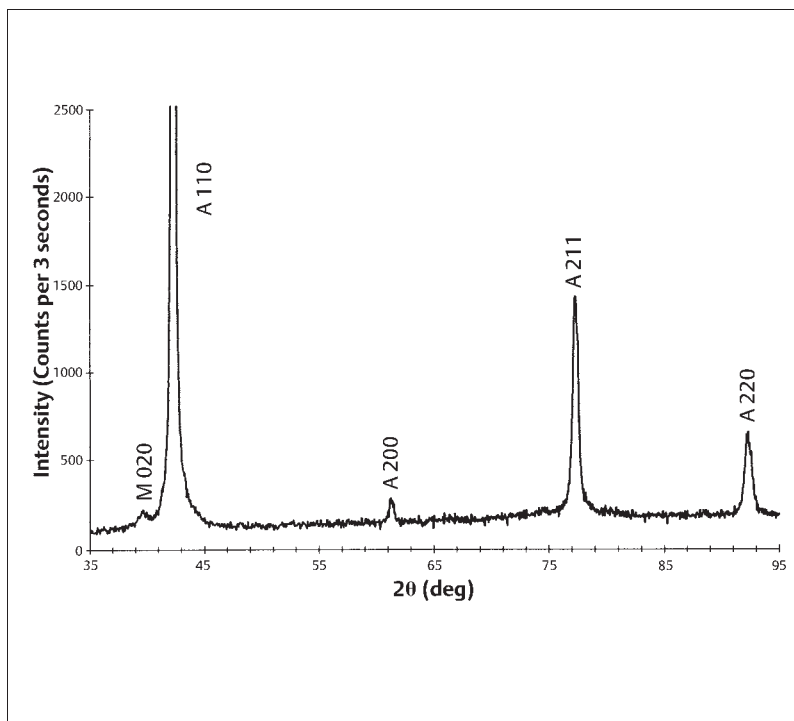
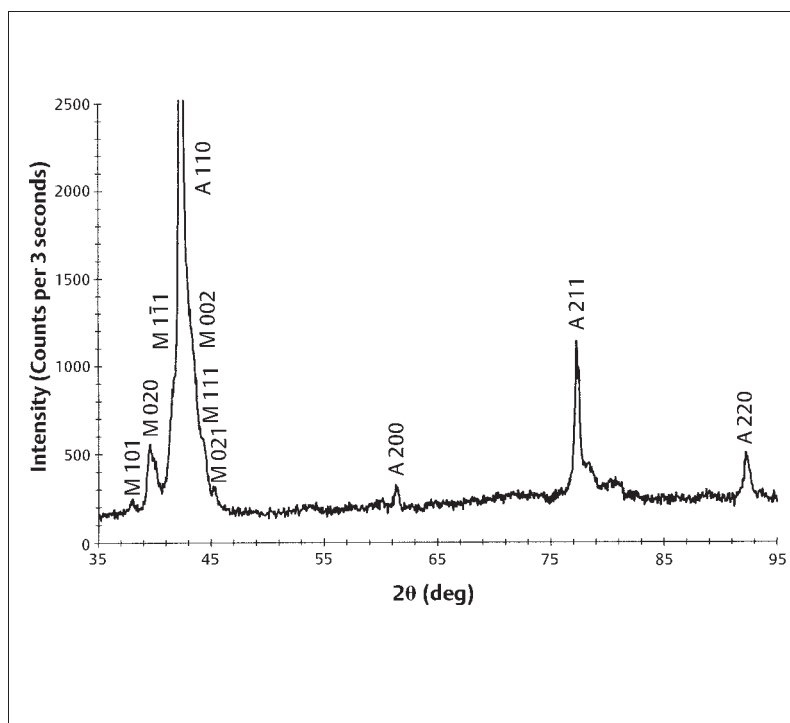


Fig. 4.19 XRD pattern for 0.016 in $\times$ 0.022 in (0.41 mm $\times$ 0.56 mm) 40 °C Copper Ni-Ti. (An abstract describing this study is found in Brantley *et al*, 1998)



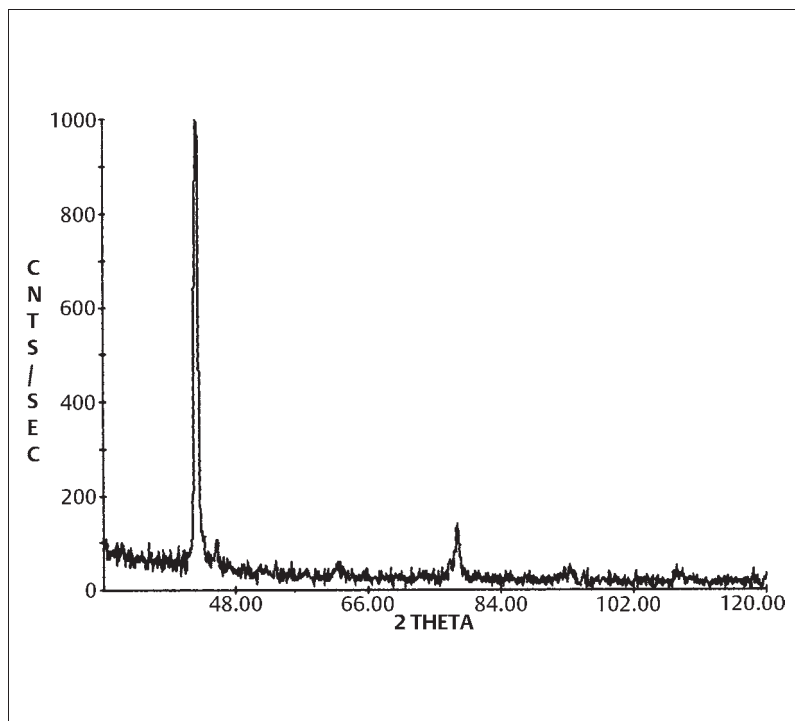


Fig. 4.20 XRD pattern for 0.016 in (0.41 mm) diameter Ni-Ti heat treated for 10 minutes at 500 °C. (From Khier, PhD dissertation, 1988)

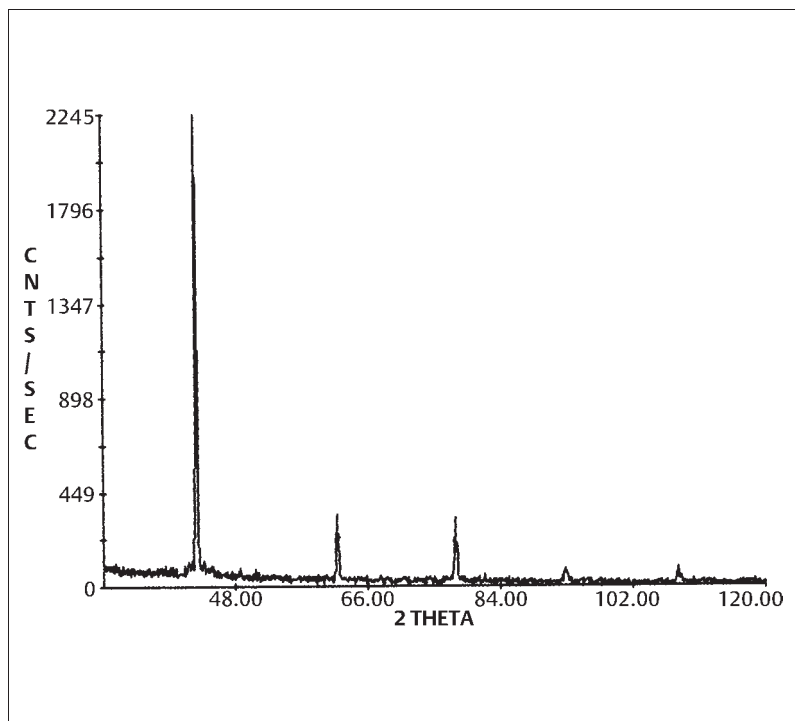


Fig. 4.21 XRD pattern for 0.016 in (0.41 mm) diameter Ni-Ti heat treated for 2 hours at 600 °C. (From Khier, PhD dissertation, 1988)

2-hour heat treatment at 600 °C also indicated that substantial stress relief had occurred, with perhaps some recrystallization of the austenite. Strong 110 preferred crystallographic orientation (Chapter 3) for the austenite is evident in Figures 4.20 and 4.21.

The X-ray diffraction pattern for Titanal after 10-minute heat treatment at 500 °C is shown in Figure 4.22. After 2-hour heat treatment at 600 °C, this nonsuperelastic wire alloy was transformed to austenite upon cooling to room temperature; Figure 4.23 shows that the austenite has a very strong 110 preferred crystallographic orientation. This indicated that, after the 600 °C heat treatment, the M_s temperature for Titanal was below room temperature. In contrast, Nitinol and another nonsuperelastic alloy (Orthonol, Rocky Mountain Orthodontics, Denver, CO, USA) retained some martensite after the 600 °C heat treatment and cooling to room temperature. This meant that the M_s temperatures for these alloys were above room temperature. Significant XRD peak sharpening for the three nonsuperelastic alloys after heat treatment at 600 °C also indicated that some recovery or recrystallization had occurred to provide stress relief.

While results from DSC and XRD analyses of the nickel-titanium orthodontic wires are qualitatively consistent, it is important to re-

member that XRD provides information about alloy phases within about 50 μm from the surface, whereas DSC provides information about phases present in the bulk specimen. Another advantage of DSC is that enthalpy changes can be measured for comparison with published values in the materials science literature. This information cannot be obtained from electrical resistivity measurements, which have been used by Chen *et al* to investigate a possible low-temperature transformation of the martensitic phase in these orthodontic wires, as previously discussed.

Experiments have suggested that measurements of Vickers hardness can also provide information about the relative proportions of the martensitic and austenitic phases in the nickel-titanium wire alloys (Table 4.4). The data in this table show that for Copper Ni-Ti the austenitic phase has higher hardness than the martensitic phase, since the hardness of the Copper Ni-Ti wires decreases on going from the 27 °C to the 40 °C variants. The highest value of hardness for Nitinol is associated with the heavily cold-worked martensitic phase in this alloy. The higher hardness for 35 °C Copper Ni-Ti compared to Neo Sentalloy arises from differences in the phase transformation temperatures and work hardening for the two alloys. The temperature of the laboratory where

Table 4.4 Values of Vickers hardness for cross sections and surfaces for several titanium-containing orthodontic wires

Alloy	Location	Vickers Hardness
27 °C Copper Ni-Ti	Surface	332 $\pm$ 7
27 °C Copper Ni-Ti	Cross Section	319 $\pm$ 17
35 °C Copper Ni-Ti	Surface	316 $\pm$ 9
35 °C Copper Ni-Ti	Cross Section	309 $\pm$ 11
40 °C Copper Ni-Ti	Surface	301 $\pm$ 8
40 °C Copper Ni-Ti	Cross Section	286 $\pm$ 5
Neo Sentalloy	Surface	286 $\pm$ 11
Neo Sentalloy	Cross Section	287 $\pm$ 19
Nitinol	Surface	428 $\pm$ 13
Nitinol	Cross Section	394 $\pm$ 11
β -titanium (TMA)	Surface	355 $\pm$ 4

An abstract describing this study is found in Brantley *et al* 1998. $N = 16$ for the surface measurements, and $N = 10 - 14$ for the cross-sectional measurements. Values of Vickers hardness are mean $\pm$ standard deviation

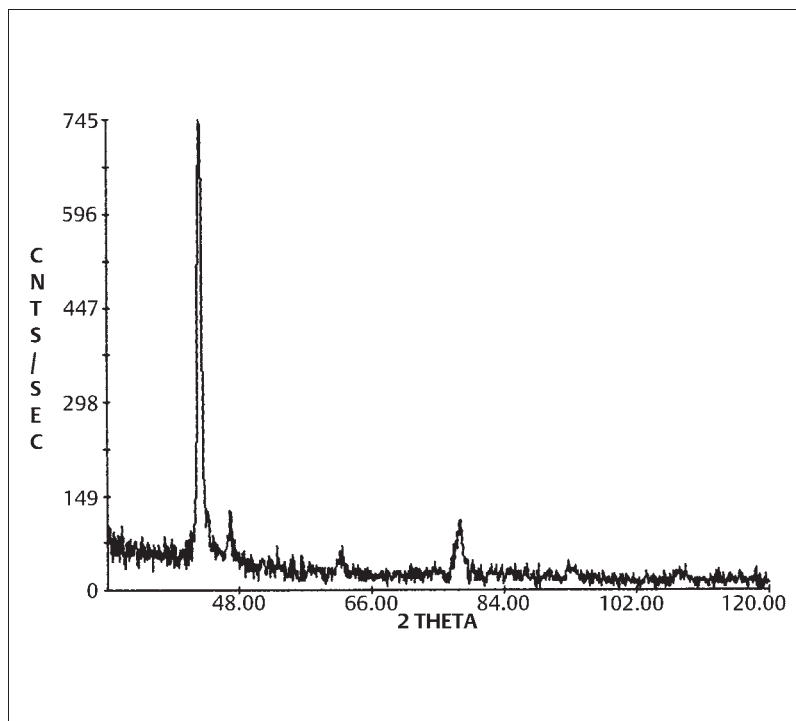


Fig. 4.22 XRD pattern for 0.016 in (0.41 mm) diameter Titanal heat treated for 10 minutes at 500 °C. (From Khier, PhD dissertation, 1988)

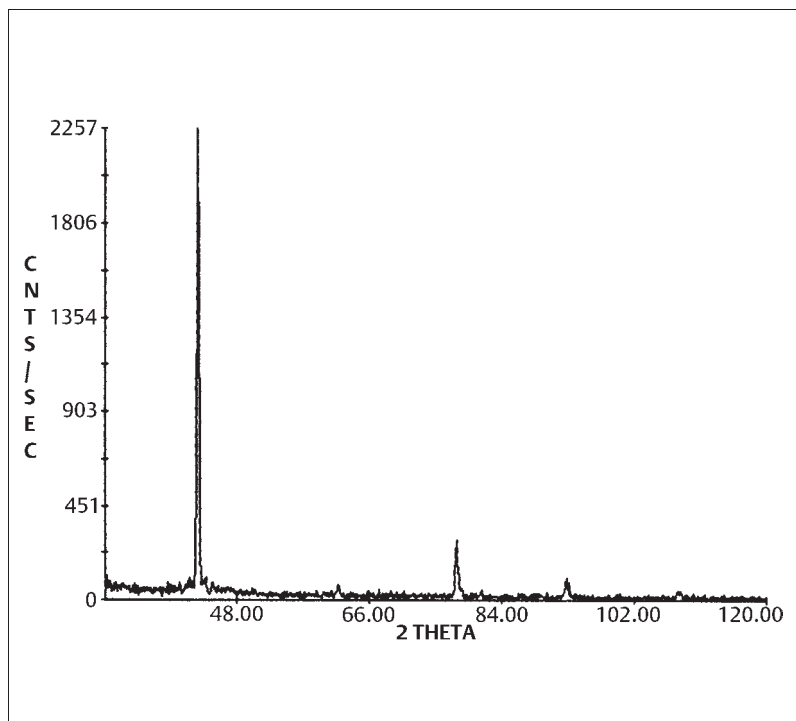


Fig. 4.23 XRD pattern for 0.016 in (0.41 mm) diameter Titanal heat treated for 2 hours at 600 °C. (From Khier, PhD dissertation, 1988)

the hardness measurements were obtained was below the A_f temperature of 35°C Copper Ni-Ti. When the temperature of the other laboratory containing the diffractometer was closer to the A_f temperature of 27°C Copper Ni-Ti, the XRD pattern for this variant more closely resembled that for Neo Sentalloy. These results demonstrate the temperature sensitivity of the phase relationships and mechanical properties of these shape-memory wires.

Table 4.4 also shows that there was no significant difference in Vickers hardness measured along the external surface or over the cross section for 27°C Copper Ni-Ti, 35°C Copper Ni-Ti and Neo Sentalloy. However, there were significant differences in Vickers hardness for the wire surface and cross section of Nitinol and 40°C Copper Ni-Ti. These results show that the likelihood of a difference in Vickers hardness at the surface and interior of the nickel-titanium wires increased with the amount of martensitic phase in the microstructure. X-ray diffraction analyses of Copper Ni-Ti and Neo Sentalloy wires have shown that the martensitic phase in these alloys has preferred orientation (Fig. 4.17–4.19), which presumably accounts for the anisotropy in Vickers hardness.

The nickel-titanium wires have relatively high surface roughness (Fig. 4.24), resulting in high archwire-bracket friction. One manufacturer (GAC International) offers an ion-im-

planted (longuard) nickel-titanium alloy, which is expected to have reduced sliding friction under clinical conditions. There is a need for future clinical studies to verify this hypothesis. While the nickel-titanium wires have optimum levels of light force delivery compared to the other single-strand wire alloys available, there is concern among some orthodontists about biocompatibility problems associated with release of nickel ions *in vivo*. In a similar manner to β -titanium, the nickel-titanium alloys achieve corrosion protection from a passivating surface film of TiO_2 . Anodic polarization experiments have shown that the breakdown potentials of these films can vary among alloys (Chapter 1), suggesting differences in their biocompatibility.

Clinical disadvantages of the nickel-titanium orthodontic alloys are that permanent bends cannot readily be placed in the wires and that the wires cannot be soldered. Heat treatment of these wires is conveniently performed by an electrical resistance technique, and a commercial apparatus (ArchMate, GAC International) allows the orthodontist to prepare custom superelastic nickel-titanium archwires for specific patients. The electrical resistance heat treatment has been exploited to produce archwires for which the level of biomechanical force varies with position (BioForce, GAC International). The effects of this direct electrical resistance heat treatment (DERHT) technique on the transformation temperatures and shape-memory behavior of several commercial martensitic-active wires have been reported.

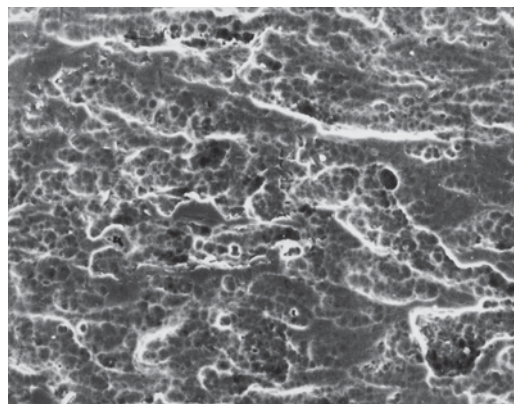


Fig. 4.24 SEM photomicrograph of the surface of an as-received Nitinol SE wire (Scale bar length = 10 μ m). (From Bradley *et al*, 1996)

Clinical Selection of Orthodontic Wires

From the preceding sections, it is evident that there is no ideal orthodontic wire alloy. Each of the four popular base-metal wires has distinct advantages and disadvantages, as summarized in Table 4.5.

The stainless steel and Elgiloy Blue wires are the least expensive, and have excellent formability and good joining characteristics. However, because of their high values of modulus of elasticity, wires manufactured from these alloys have the highest force delivery, along with lower elastic ranges and springback compared to the two titanium-containing wire alloys.

Table 4.5 Summary of relative levels of important properties for selection of orthodontic wire alloys

Property	Stainless Steel	Cobalt-Chromium-Nickel (Elgiloy Blue)	β -Titanium (TMA)	Nickel-Titanium
Cost	Low	Low	High	High
Force delivery	High	High	Intermediate	Light
Elastic range (springback)	Low	Low	Intermediate	High
Formability	Excellent	Excellent	Excellent	Poor
Ease of joining	Can be soldered. Welded joints must be reinforced with solder.	Can be soldered. Welded joints must be reinforced with solder.	Only wire alloy that has true weldability.	Cannot be soldered or welded.
Archwire-bracket friction	Lower	Lower	Higher	Higher
Concern about biocompatibility	Some	Some	None	Some

Because the stainless steel and Elgiloy Blue alloys do not bind significantly to the dies or rollers during processing, orthodontic wires manufactured from these alloys have the smoothest surfaces, resulting in relatively low archwire-bracket friction. Both alloys contain substantial amounts of nickel, which has caused some concern among orthodontists about their biocompatibility. However, extensive clinical use of these wire alloys for several decades suggests that such problems are minimal.

Orthodontic wires fabricated from β -titanium (TMA) are generally more expensive, than those manufactured from the other three popular alloys. However, there is no concern about biocompatibility of the β -titanium wires, since there is no nickel in the alloy composition. The β -titanium wires have force delivery and elastic range and springback values intermediate to those for the stainless steel and Elgiloy Blue wires and the nickel-titanium wires. Consequently, the orthodontist may select β -titanium archwires that will more nearly fill the bracket slots compared with the wire sizes that would be selected for stainless steel or Elgiloy Blue wires. The outstanding formability of the β -titanium alloy gives the orthodontist the capability of fabricating archwires or segments with complicated loop configurations not possible using the nickel-titanium alloys.

Burstone and Goldberg have provided several clinical examples where the use of β -titanium wires offers advantages to the orthodontist. These include the alignment of teeth in an arch during finishing, the rotation and changing of the axial orientation of teeth, the use of specialized springs or auxiliaries such as an intrusive arch or a canine root spring, and the fabrication of closing loops that may contain helices. The weldability of TMA is very useful when assembly of a complex appliance is needed.

A recent clinical study has reported that the rate of orthodontic space closure was not significantly different for ion-implanted and conventional (not ion-implanted) TMA wires, and that the rate of closure was similar to that reported for stainless steel archwires. Additional clinical studies are needed to investigate the clinical efficacy of the ion-implanted β -titanium archwires.

Very recently, a new β -titanium archwire (Resolve) has been introduced by GAC International. Research is needed to investigate the differences in mechanical properties, ease of manipulation, and clinical performance of the Resolve and TMA β -titanium alloys.

The nickel-titanium wires have the lightest force delivery and widest elastic range of the four popular alloys, along with outstanding springback, particularly for the shape-memory alloys. However, these wires are expensive,

have poor formability, and cannot be soldered or welded. Nevertheless, the nickel-titanium wires find application in a variety of clinical cases because of their excellent elastic range and springback. Archwire-bracket friction is comparably high to that for β -titanium because of the relatively rough wire surfaces that arise from the high titanium content. However, clinical studies have not been performed to determine whether the higher sliding friction significantly increases the duration of patient treatment compared to that with ion-implanted nickel-titanium and β -titanium wires and with stainless steel wires.

Andreassen and Morrow emphasized the benefit of rectangular Nitinol archwires for early treatment stages, where simultaneous rotation, tipping, leveling, and torquing could be performed. They pointed out that in some cases treatment can begin with full-size rectangular wires that nearly fill the bracket slot. Clinical examples, such as crossbite correction, uprighting impacting canines, and opening bites where the use of Nitinol was advocated would be equally applicable to the other nickel-titanium wires. The superelastic and shape-memory nickel-titanium wires are particularly useful where large deflections are necessary for badly malpositioned teeth. Orthodontic appliances fabricated from these wires will generate the most nearly constant forces during the major stages of tooth movement. However, it should be noted that force levels exerted *in vivo* may not reach the superelastic plateau, and thus the force would not be independent of deflection.

Superelastic nickel-titanium coil springs, originally developed for orthodontics by Miura and colleagues, have found wide applicability. The force generated by the coil spring depends upon the wire diameter, lumen size, pitch of the open spring, and the martensite transformation temperature. These springs can exert constant light, continuous force over a very wide range, providing an optimal appliance for tooth movement under appropriate clinical conditions. While an *in vitro* study using a saliva substitute at 37 °C indicates that some force degradation occurs with closed coil springs over time, this force decay is much less pronounced than that for the elastomeric modules (Chapter 8). Another study has shown that the force delivery of the superelastic coil springs

can be substantially affected by small changes in temperature, which may have clinical importance for some patients. Laboratory investigation has established that interaction of the coil spring with a stainless steel guiding archwire for molar distalization can result in substantial frictional loss of the spring-generated force.

While the preceding discussion has focused on the metallurgy and clinical applications of single-strand orthodontic wires, Burstone has pointed out that multistrand wires can be used advantageously in a variety of applications. These include initial torque control, a transition between round and rectangular wires, and a finishing wire at the end of treatment. Oltjen *et al* have reported the effects of wire size, number of strands and amount of deflection on the stiffness for a variety of multistrand wires. Another study has found that very low frictional forces exist when multistrand wires are used. A evaluation of the clinical performance of aligning archwires found no significant difference among two nickel-titanium wires and one multistrand stainless-steel wire. It was hypothesized that during the initial tooth alignment phase of routine orthodontic treatment there may be insufficient deformation of NiTi wires to take advantage of their superelastic behavior. A clinical trial comparing the use of multistrand stainless steel, superelastic NiTi, and ion-implanted superelastic NiTi wires for initial tooth alignment also found no significant differences among the archwires, with all three providing effective tooth movement. Aesthetic bonded orthodontic retainers for long-term clinical use have been fabricated from multistrand wires and composite resins.

Laboratory measurements on archwires of several stainless steel alloys, Elgiloy Blue and Green, and Nitinol have shown that force relaxation ranging from about 5 % to 13 % occurs over a 28-day period at 21 °C. The time dependence followed a semilogarithmic relationship, but these levels of force loss would not be expected to have clinical significance. Heat treatment of the Elgiloy Green archwires eliminated the force relaxation, as did testing of Nitinol at 37 °C. Subsequently, a study of the effect of storage for 1 to 4 months in three buffered saline solutions of varying pH revealed modest changes in the mechanical properties of Nitinol. The average decreases of 18 % in the modulus of

elasticity and 10% in the yield strength measured in tension would likely have little clinical significance. Further laboratory investigation of the effect of long-term deflection for periods up to four weeks showed that there was no clinical

significant difference in the permanent deformation after deactivation for several commercial nickel-titanium wires, which exhibited better springback and less permanent deformation than stainless steel and TMA wires.

Future of Orthodontic Wires

There have been efforts to produce esthetic orthodontic wires to complement the ceramic brackets. A transparent nonmetallic orthodontic archwire with a silica core, a silicon resin middle layer, and a stain-resistant outer layer (Optiflex, Ormco) was described by Talass. Although the brittle core prevents the placement of sharp bends by the orthodontist, this composite wire is highly resilient. Kusy reported that a fluorocarbon-coated, white-colored, triple-stranded stainless-steel wire (Eastman Dental, New Brunswick, NJ, USA) does not withstand the mechanical forces and enzyme activity in the oral environment. Kusy and his colleagues have developed an archwire containing S2 glass fibers (Owens Corning, Toledo, OH, USA) embedded in a polymeric matrix formed from Bis-GMA and TEGDMA (Chapter 9); benzoin ethyl ether is present as a uv (ultraviolet) photoinitiator. By adjusting the ceramic/polymer proportions, these wires can be manufactured in a wide range of clinically relevant levels of elastic stiffness, using the technique of photo-pultrusion with ultraviolet light illumination to cure the polymer matrix. Rectangular cross-sections

and preformed archwires can be fabricated, and the surface chemistry can be modified to provide enhanced biocompatibility and low coefficients of sliding friction. Poly (chloro-p-xylylene) coatings have been found to minimize glass fiber release during manipulation of the wires. This group has also developed a composite ligature wire consisting of ultra-high molecular weight polyethylene fibers in a poly (n-butyl methacrylate) matrix. A research group at the University of Hokkaido (Japan) has developed an archwire with a poly (methylmethacrylate) matrix reinforced by $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ fibers that are reported to be biocompatible. Laboratory mechanical testing results for composite archwires developed by both research groups have been promising and warrant further investigation into their clinical use. Watanabe *et al* have described a polyethylene terephthalate wire for maxillary retainers. Another area of potential interest is the use of true shape-memory polymers for orthodontic wires. Thus, exciting research directions exist for the development of entirely new nonmetallic orthodontic wires with engineered properties.

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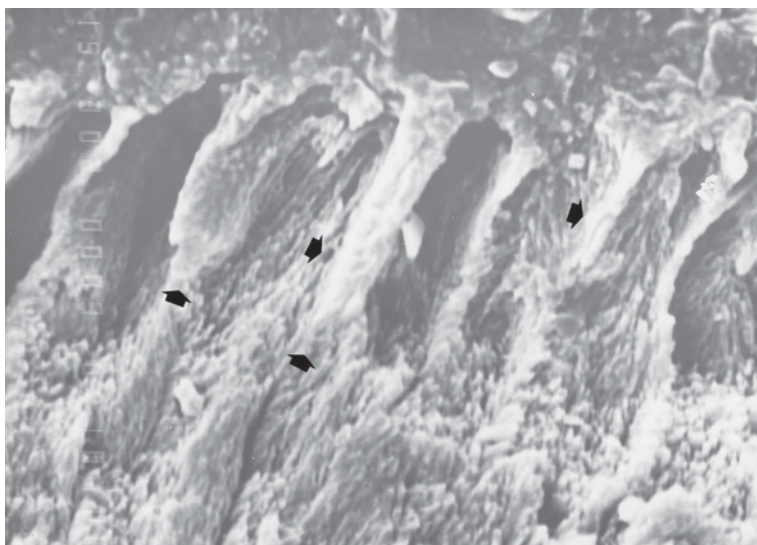
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5 Enamel Etching and Bond Strength

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Secondary electron image of a sectioned interface between an orthodontic adhesive and phosphoric acid-etched enamel. Original magnification $\times 3000$

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Introduction

Direct bonding and indirect bonding of orthodontic brackets typically utilize a resin composite adhesive and require that the enamel be etched, whereas orthodontic bands are usually cemented with glass-ionomer cement without etching of tooth structure. Bond failure of brackets or bands is one of the most frustrating occurrences in an orthodontic practice. Consequences of bond failure can include increased treatment time, additional costs in materials and personnel, and unexpected additional visits by the patient. Understanding various characteristics of human enamel assists the orthodontist in the proper preparation of the tooth surface, and in selection and application of appropriate orthodontic cements/adhesives. Knowing the location of a bond failure allows the ortho-

dontist to modify his or her bonding technique and to counsel patients on care of their appliances. This chapter will describe the characteristics and preparation of enamel for bonding of brackets and the results of laboratory and clinical testing of debonding force and bond strength for current adhesives.

The composition, properties, and applications of zinc phosphate, zinc polycarboxylate, glass-ionomer, hybrid ionomer, compomer, and resin composite orthodontic cements/adhesives will be discussed at length in Chapters 10 and 11. In this chapter, bond testing and bond strengths of these materials for the retention of brackets and bands to enamel will be discussed; included in this discussion will be the effects of metal, ceramic, and plastic brackets on bonding to enamel.

Effects of Important Variables on Bond Strength

Differences among Teeth

Differences in bond strength are generally not observed among central incisors, first premolars, or third molars. Likewise, no differences in bond strength are observed between lingual and buccal surfaces. One study recommends a 15-second etch for premolars, canines and anterior teeth and a 30-second etch for first molars. Older permanent teeth tend to produce slightly higher bond strength than younger permanent teeth.

Effects of Fluoride

The presence of fluoride ions is the main factor associated with mottled enamel. The ingestion of fluoride can damage both the ameloblast and the matrix. Fluorosis is revealed as a diffuse bilateral white opacity that covers the enamel. Long-time ingestion of fluoride accentuates the appearance of the perikymata and is associated with changes in color, depending on dose, timing, and duration of fluoride ingestion. The characteristic brownish color of the enamel in severely fluorosed teeth occurs after eruption. Surface enamel fluorosis differs from

non-fluoride-induced opacities, which are generally well demarcated and asymmetrically distributed. Fluorosed enamel shows various degrees of hypomineralization.

Teeth with a higher concentration of fluoride are generally considered more resistant to acid etching than normal teeth and may require an extended etching time. Bond strengths to a group of severely and moderately fluorotic teeth, even with additional time for acid etching, were about 40 % lower than bond strengths to normal teeth, although a group of mildly to moderately fluorotic teeth from young adults showed similar bond strengths when compared to normal teeth.

Clinically, the etching of enamel creates microporosity within the enamel (Fig. 5.1) and reduces surface tension that allows the resin to penetrate and polymerize within the etched enamel rods. Standard 37 % phosphoric acid typically dissolves about 5–10 μm of enamel surface and creates a zone of etched enamel rods for about 15–25 μm . The etching process creates calcium monophosphate and calcium sulfate by-products that must be removed by a vigorous water rinse. Care must be taken to lightly dab the enamel surface with the acid etchant to avoid polishing or fracturing the exposed en-

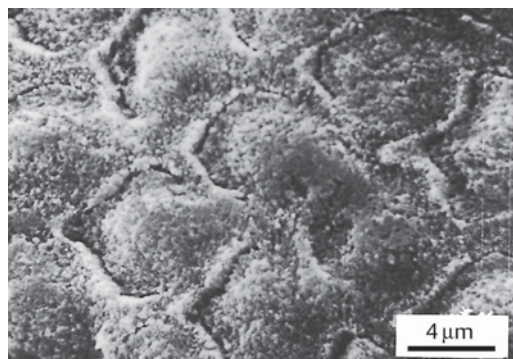


Fig. 5.1 Typical etching pattern of human enamel showing enamel rods with microporosities. (From Faust *et al*, 1978)

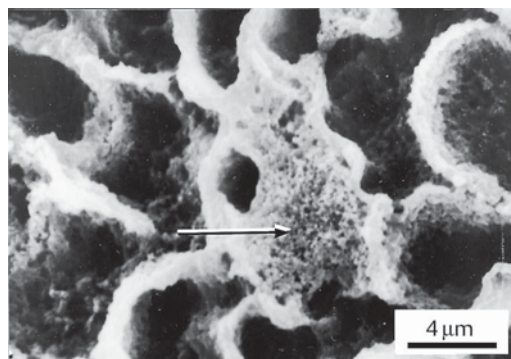


Fig. 5.2 Re-etched human enamel prepared for rebonding after bond failure. Retained fragments of resin composite adhesive are indicated by the arrow. (From Faust *et al*, 1978)

amel rods. After bond failure, teeth can be prepared for rebonding. Scanning electron microscopic observations have revealed retained fragments of composite adhesive on the enamel (Fig. 5.2).

Type and Concentration of Acid

In restorative dentistry the highest possible bond strength to tooth structure is desirable. In contrast, the orthodontic bond strength must be sufficient to retain the brackets but low enough to allow easy clean-up of adhesive when the case is completed and the brackets are removed. Some factors that influence acid etching of enamel include the type and concentration of the acid and the time of etching.

Etching with 10% or 37% phosphoric acid produces the highest bond strengths (28 MPa) to enamel. The use of 10% maleic acid for etching results in a lower bond strength (18 MPa), and no etching yields a very low bond strength. No differences in bond strengths are observed when enamel is etched with phosphoric acid ranging in concentration from 2% to 37%. One study reported that 2% phosphoric acid etchant was adequate for bonding, whereas another recommended 10–30% phosphoric acid.

Duration of Etching

No differences in bond strength are detected between 15-second and 60-second etching with 37% phosphoric acid; however, shorter etching times cause less enamel damage on debonding. Decreasing etching time between 30 and 10 seconds does not affect bond strength (11 MPa) or location of failure site, whereas etching for 0 or 5 seconds reduces bond strength (less than 3 MPa) significantly. Scanning electron microscopy shows that etching with 37% phosphoric acid for at least 30 seconds produces more optimal etching patterns than etching for 15 seconds.

Etching vs. Not Etching

Resin composite does not bond well to unetched enamel; however, hybrid ionomer orthodontic cements have bond strengths to moist, unetched enamel ranging from 8 to 25 MPa. Hybrid ionomer orthodontic cements presently bond better to moist, unetched enamel than to sandblasted metal brackets. Once their bond strength to metal brackets is improved, these cements could be used in a non-acid-etching bonding technique. Tables 5.1 and 5.2 show the performance of resin composite adhesive and hybrid ionomer cement.

Table 5.1 Comparison of relative properties of cements and adhesives used for orthodontic bonding and banding

Cement/Adhesive	Bond Strength to Enamel	Bond Strength to Metal Brackets
Resin composite (Transbond)	High	Medium-high
Hybrid ionomer (Fuji Ortho LC)	Medium-high	Low-medium

Table 5.2 *In vitro* tensile bond strengths of hybrid ionomer and resin composite orthodontic adhesives to un-etched enamel and sandblasted metal brackets

Substrate	Bond Strength (MPa)					
	AD	FO	FLC	VB	VM	CO
Unetched enamel	10	25	15	13	8	0
Sandblasted metal bracket	6	4	5	2	3	7

Adapted from Powers *et al*, 1996. Hybrid ionomers: AD = Advance, FO = Fuji Ortho, FLC = Fuji Ortho LC, VB = Vitrebond, VM = Vitremer. Resin composite: CO = Concise

Use of Pumice with or without Fluoride

Pumice or a prophylactic paste is often used to clean the enamel surface before acid etching and bonding. However, bond strength appears to be unaffected whether pumice is used or not. Use of a fluoridated pumice or paste with varying fluoride concentrations also does not affect bond strength or location of bond failures.

Iatrogenic Effects of Etching

While most clinicians accept acid etching of enamel as a routine technique, there are some

Table 5.3 Possible iatrogenic effects of acid etching of enamel

- Fracture and cracking of enamel upon debonding
- Increased surface porosity – possible staining
- Loss of acquired fluoride in outer 10 μm of enamel surface
- Loss of enamel during etching
- Resin tags retained in enamel – possible discoloration of resin
- Rougher surface if over-etched

possible iatrogenic effects (Table 5.3). Acid etching of enamel removes about 10–20 μm of enamel. Etched enamel is porous, making it susceptible to retention of stains, although the porosities are filled by precipitates from saliva over time. Even the most careful debonding technique causes fracture of small enamel fragments and cracks. An additional 6–50 μm of enamel is estimated to be lost on debonding. Another concern is that the resin tags that remain in the enamel after debonding may change color with time.

Crystal-Growing Solutions

A proposed alternative to etching enamel for retention of an adhesive is to grow crystals on the enamel surface. This technique is called crystal bonding. Potential advantages of crystal bonding include easier debonding, less residual adhesive left on the tooth and less damage to enamel. Crystal bonding involves application to enamel of a poly(acrylic acid) solution containing sulfate ions, which causes growth of calcium sulfate dihydrate crystals on the enamel surface. These crystals in turn retain the adhesive. Since crystal bonding produces bond strengths of 60–80% of the bond strength obtained with acid etching, it is not yet considered a practical technique.

Acidic Primers

Another alternative to etching enamel with phosphoric acid is to use an acidic primer of the type used to bond restorative composites to enamel and dentin. Although these primers are expensive, comparable bond strengths are found.

Air Abrasion

Air abrasion, also referred to as micro-etching, is a technique in which particles of aluminum oxide are propelled against the surface of enamel or another substrate by high air pressure, causing abrasion of the surface. Some manufacturers of commercial units have suggested that air abrasion could eliminate acid etching; however, bond strengths to air-abraded enamel are only about 50% of those to acid-etched enamel. As will be discussed subsequently in this chapter, air abrasion or micro-etching of metal brackets or bands is an effective technique for improving bond strength to these air-abraded substrates. Air abrasion could be an alternative to pumicing the teeth before etching.

Laser Etching

The application of laser energy to an enamel surface causes localized melting and ablation. Removal of enamel (etching) results primarily from the micro-explosion of entrapped water in the enamel. In addition, there may be some melting of the hydroxyapatite crystals. Laser etching of enamel by a neodymium-yttrium-aluminum garnet (Nd:YAG) laser typically produces lower bond strengths than does acid etching. Satisfactory *in vitro* bond strengths were obtained in one study only when the Nd:YAG laser was used for 12 seconds at maximum power (3 W). Studies of CO₂ laser (pulsed mode) etching of enamel have shown that bond strengths of 10 MPa can be obtained reliably. The thermal effects of laser etching on the enamel substructure require further research.

Moisture-Resistant Primers

An alternative to bonding to dry enamel is to apply a moisture-resistant primer (Transbond MIP, 3M/Unitek, Monrovia, CA, USA) to etched enamel that has been contaminated with moisture or saliva. This type of primer is a hydrophilic methacrylate monomer that will wet enamel contaminated with saliva or moisture. The bond strength of a resin composite adhesive applied to enamel primed with the moisture-resistant primer is similar to that of resin composite adhesive applied to etched, dry enamel. Adhesives that are reported to have acceptable performance in a moist environment and recently introduced moisture-active adhesives that require the presence of moisture for proper polymerization are discussed in detail in Chapter 10.

Chlorhexidine

Chlorhexidine can be applied on the teeth and over orthodontic appliances during treatment to reduce bacterial colonization. Bond strength is not affected if the chlorhexidine is applied after bonding has been completed or as a prophylactic paste on enamel before etching. Bond strength is reduced to an unacceptable level, however, if the chlorhexidine is applied as a layer on etched enamel or on the sealant before the adhesive is applied. A chlorhexidine-containing primer did not significantly affect bond strength.

Bleaching

Teeth recently bleached have been observed to have significantly lower bond strengths to resin composites. The bleach produces oxygen, which inhibits free radical polymerization of resin composites. Research has shown that orthodontic brackets can be placed after use of carbamide peroxide bleaching with no adverse effect on bond strength.

Measurement of Debonding Force and Bond Strength

With numerous adhesives and orthodontic band and bracket materials available, *in vitro* measurements of debonding force and bond strength play an important role in characterizing the bonding potential of new systems. The first goal of bond testing is to measure the force of debonding. The second goal is to observe the location of the bond failure.

Debonding Force

The debonding force for brackets has been reported in the research literature in units of newtons (N), kilograms (kg), or pounds (lb). If the average force transmitted to a bracket during mastication is between 40 and 120 N, then a desirable level of bracket adherence to enamel would require a force greater than 120 N (12.2 kg or 5.6 lb) to cause debonding. The reporting of force for bond failure can be misleading if there are substantial differences in the bonding areas of the brackets tested. To properly compare brackets with bases of differing geometries, it is necessary to determine the bond strength, as described in Chapter 2.

Bond Strength

Bond strength, which is the force of debonding divided by the area of the bonded interface, is commonly reported in the orthodontic literature. Publications have reported the bond strength in units of megapascals (MPa), kilograms per square centimeter (kg/cm^2), and pounds per square inch (lb/in^2 or psi). If a typical bracket has a nominal bonding area of 16 mm^2 and the force of debonding is 120 N, then the bond strength will be $7.5 \text{ N}/\text{mm}^2$ or 7.5 MPa, as previously described in Chapter 2.

An adhesive-bracket system should be able to withstand a stress of at least 6–8 MPa. To improve retention through a larger bonding area, a larger bracket or band should be selected or the bracket/band should be micro-etched before placement.

Bond Failure

Adhesive failures are those that occur between the cement and the tooth or between the cement and the bracket or band (Chapter 1). Cohesive failures can occur within the tooth, within the cement or even within the bracket. Often, bond failures are a mixture of adhesive and cohesive failures. The percentages of the types of bond failure can be measured using a scale such as the Adhesive Remnant Index. This index specifies the amount of cement remaining on the tooth and bracket or band.

For example, a hypothetical bond strength experiment (Table 5.4) found that cement A had 100% adhesive failures at the enamel/cement interface, whereas cement B had 100% cohesive failures in the cement. In this experiment, the bond strength of cement A was lower than its cohesive strength and the cement separated cleanly from the tooth. The relatively low bond strength of cement A might suggest that this cement bonds poorly to enamel or that the enamel surface was contaminated, resulting in an inferior bond. In contrast, there was cohesive failure in cement B, and the relatively high value of bond strength demonstrated that this cement bonded well to enamel. However, under clinical conditions high bond strength with cohesive cement failure means that increased effort must be expended to remove the retained cement from the enamel surface.

Table 5.4 Data obtained from a hypothetical *in vitro* tensile bond strength experiment involving two orthodontic adhesives bonded to enamel

Adhesive	Bond Strength (MPa)	Failure site
A	5	100 % adhesive
B	16	100 % cohesive

Bond Strength Measurement by Shear and Tensile Testing

Bond strength testing is typically performed in shear or tension, using a screw-driven or servohydraulic universal testing machine (Chapter 2), although torsional testing has been reported. In shear testing, the bonded bracket is loaded by a blade in tension or compression or by a wire loop in tension, so that the bracket slides parallel to the enamel surface. Pure shear loading is difficult to achieve, and most shear testing also includes components of peeling, tension, and torsion. In tensile testing the bracket is pulled perpendicularly from the enamel substrate. Both shear and tensile loading modes are valid tests for studying bond strengths of orthodontic materials. The goal in bond testing should be to achieve a coefficient of variation [(standard deviation/mean) $\times 100\%$] in the range 20–30%. Typi-

cally, tensile testing produces a lower coefficient of variation than the most common shear tests.

Bond testing using teeth involves many variables that can affect the measured bond strength. These variables include: (1) type of tooth (e.g., incisor, molar, human, bovine); (2) fluoride content of tooth; (3) disinfection and storage media of tooth before bonding; (4) elapsed time of storage following bonding; (5) type of loading (shear, tension, torsion, or peeling); (6) configuration of specimen testing jig; (7) crosshead speed of mechanical testing machine; and (8) bonding area of the bracket. Unfortunately, no specifications (American National Standards Institute/American Dental Association or International Organization for Standardization) currently exist to standardize testing protocols for orthodontic bond strength measurements.

Experimental Models for Evaluating Bond Strength

Bond strength in orthodontics can be evaluated using prospective or retrospective clinical models or *in vitro* using simulated clinical models or bonding to a standardized substrate. A more fundamental test is the isolated substrate model, in which bonding of an adhesive to tooth structure or a bracket is studied independently.

Clinical Simulation Model

In this model, brackets are bonded to extracted human or bovine teeth, and *in vitro* debonding occurs in shear or tension. The advantage of this model is that both the tooth and bracket are present, so the test appears to be clinically relevant. The disadvantage is that often bond failures occur at both interfaces, so it is difficult to isolate the weak link in the tooth-adhesive-bracket system. Less frequently, brackets have been bonded clinically to human teeth before planned extraction and then tested after extraction.

Isolated Interface Model

In this model, the interface between the tooth or restorative material and the adhesive is studied separately from that between the bracket or band material and the adhesive. To study the tooth-adhesive interface, a cylinder or cone of adhesive is bonded directly to the enamel surface and then debonded (Fig. 5.3). To study the bracket-adhesive interface, the bracket is bonded to the adhesive, which is retained in an acrylic well or bonded to a flat acrylic surface. This model is particularly applicable for studying metal brackets, for which failure at the bracket-adhesive interface is common, thereby reducing the need for extraction of teeth.

Bonding to a Standardized Substrate

Most investigators use human enamel, bovine enamel, or an acrylic surface as a test substrate. A commercial glass-ceramic has been studied as an alternative to enamel. Both shear and ten-

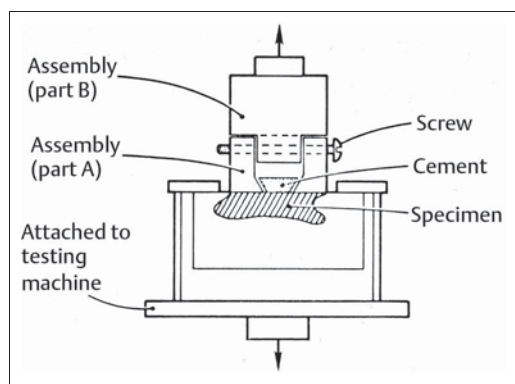


Fig. 5.3 Test assembly (isolated interface model) for debonding adhesive from human enamel in tension. (From Barakat and Powers, 1986)

sile bond strengths determined after 24 hours with the glass-ceramic were equivalent to those measured with human enamel; however, the adhesives bonded to the glass-ceramic did not survive well after thermocycling.

Clinical Studies

The randomized clinical trial is an experimental study in which the investigator selects and controls the treatments under study in order to draw conclusions about whether a particular treatment produces an effect. The converse of the prospective study is the retrospective (observational) study, which involves the examination of previous treatment records to obtain data for analysis. The investigator thus obtains research data by observing treatment events without controlling them. Advantages and disadvantages of prospective and retrospective clinical studies are summarized in Table 5.5.

Clinical Bracket Retention

Clinical bracket retention is typically determined retrospectively or prospectively as the failure rate, defined as the number of brackets that failed over the study period divided by the number of brackets bonded. Bracket failures caused by known operator error are often excluded from the calculation. More sophisticated survival analysis allows the time occurring before failure and excluded (censored) information to be considered. Bond strengths also have been measured *in vivo* over short periods of time, using a hand-held dynamometer.

Clinical variables that can affect bracket failure rate include: age and sex of patient, treatment mechanics, operator, and tooth type. Standardized protocols for clinical testing of orthodontic adhesives, bands, and brackets do not exist.

Bonding of Brackets to Enamel – *in vitro* Studies

The most commonly used orthodontic adhesive for direct and indirect bonding of brackets to enamel is resin composite. Other cements that have been used with different degrees of success include acrylic resin, compomer, hybrid ionomer and glass-ionomer. These adhesives are discussed at length in Chapters 9, 10 and 11. Metal brackets are the most popular, but with the increasing interest in aesthetics by patients, ceramic and plastic brackets are in widespread use. The composition and structure of the bracket can affect the bonding of the adhesive and can subsequently affect the bonding of the adhesive to enamel. Detailed information about brackets is provided in Chapter 7.

Table 5.5 Summary of advantages and disadvantages of prospective and retrospective clinical studies

Type of Study	Advantages	Disadvantages
Prospective	Randomization reduces bias Conclusions may be stronger	Patients lose choice of treatment Patients may drop out of study Ethical concerns if one treatment is perceived as inferior
Retrospective	Minimal expenses Easy to perform (record review)	Variations in patients may cause confounding effects Interpretation of charts (possible bias)

Effects of Metal Brackets

The filler content of resin composites affects the *in vitro* bond strength to brackets that depends on mechanical retention. Highly filled resin composites bond to metal brackets with mechanical retention better than do slightly filled composites; the same bond strengths have been found for some ceramic and plastic brackets (Table 5.6). Bond strength of adhesives to new metal brackets is lowered by spot welds and broken mesh areas, which lead to stress concentrations (Fig. 5.4). Hybrid glass-ionomer cements used with metal

brackets have bond strengths much lower than resin composites and similar to conventional glass-ionomer cements, and require careful patient selection for direct bonding.

The bond strength for resin composite is affected by the adhesive thickness between the bracket and substrate (Table 5.7). A variety of bracket pretreatments such as micro-etching, silanating and activation are available to improve the bonding of resin composite adhesives to metal brackets (Table 5.8). Other metal adhesion strategies (sandblasting, sandblasting and silanating, silica coating) provide modest increases in bond strengths of resin

Table 5.6 Typical *in vitro* tensile bond strengths of direct-bonding orthodontic adhesives to ceramic, metal, and plastic brackets

Adhesive	Bond Strength (MPa)		
	Ceramic Bracket	Metal Bracket	Plastic Bracket
Resin composite, highly filled	5	13	8
Resin composite, slightly filled	5	9	8
Hybrid ionomer	6–7	3–4	1–4

Adapted from Blalock and Powers, 1995; Buzzitta *et al*, 1982; de Pulido and Powers, 1983

Table 5.7 *In vitro* tensile bond strengths of chemically cured and paste-primer resin composite orthodontic adhesives as a function of thickness (mm) between the bracket and substrate

	Bond Strength (MPa)			
	0.00 mm	0.25 mm	0.30 mm	0.33 mm
Chemically cured	4	8	8	8
Paste-primer	9	3	3	0

Adapted from Evans and Powers, 1985

Table 5.8 *In vitro* tensile bond strengths of a resin composite orthodontic adhesive to different types (mesh, photo-etched, grooved) of treated metal brackets

Treatment	Bond Strength (MPa)		
	Mesh base	Photo-etched base	Grooved base
No treatment	8	8	9
Silanation	11	9	9
Etching	8	8	15
Activation	9	9	10
Etching and silanation	10	8	11
Etching and activation	8	8	12

Adapted from Siomka and Powers, 1985

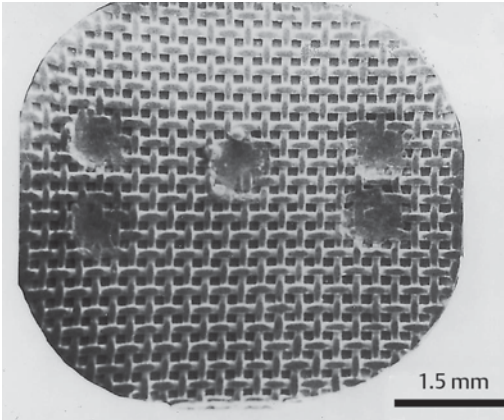


Fig. 5.4 Spot welds and broken mesh on the base of a metal bracket could cause high stress concentration in an adhesive. (From Dickinson and Powers, 1980)

Table 5.9 *In vitro* tensile bond strengths of a resin composite orthodontic adhesive to different types of reconditioned metal brackets prepared for re-bonding

Treatment or Condition of Bracket Base	Bond Strength (MPa)
New bracket	10
Ground to metal with green stone	6
Ground away resin adhesive with green stone	5
Chemical reconditioning	7
Thermal reconditioning	8

Adapted from Wright and Powers, 1985

composite to metal brackets. Sandblasting (micro-etching or air abrasion) of metal brackets using aluminum oxide particles improves the bond strengths of glass-ionomer and hybrid ionomer adhesives to the metal.

Recycling or rebonding of metal brackets generally results in lower bond strengths when compared to new brackets (Table 5.9). Sandblasting (micro-etching or air abrasion) of failed metal brackets, however, produces satisfactory bond strengths.

Effects of Ceramic Brackets

Retention of adhesives to ceramic brackets can be mechanical or chemical or both (Table 5.10). Mechanical bonding requires indentations or undercuts in the bracket base, a roughened surface created by micro-abrasion (sandblasting or micro-etching) (Table 5.11), or roughness caused by chemical etching with a 9.6% hydrofluoric acid (HF) gel. One bracket (Transcend 2000, 3M Unitek) uses fused aluminum oxide particles to provide increased surface area and greater retention of the adhesive. Chemical bonding requires treatment of the ceramic bracket base with silane. One end of the silane molecule bonds to the ceramic, while the other end bonds to the carbon-carbon double bonds available from the resin composite adhesive (Chapters 7 and 9). Restorative hybrid ionomers have bond strengths similar to those of resin composites when used with ceramic brackets and are considered adequate for clinical use.

Bond strengths of a variety of single-crystal and polycrystalline alumina ceramic brackets

Table 5.10 *In vitro* tensile bond strengths of hybrid ionomer and resin composite orthodontic adhesives to ceramic, metal, and plastic orthodontic brackets

Bracket Type	Bond Strength (MPa)	
	Hybrid Ionomer Adhesive	Resin Composite Adhesive
Ceramic (mechanical)	6	7
Ceramic (silanated)	7	7
Ceramic (polycarbonate base)	4	7
Metal	4	6
Plastic	1	10

Adapted from Blalock and Powers, 1995

Table 5.11 *In vitro* tensile bond strengths of glass-ionomer and hybrid ionomer orthodontic adhesives to micro-etched stainless steel orthodontic bands

Bracket Type	Bond Strength (MPa)	
	Glass Ionomer Adhesive	Hybrid Ionomer Adhesive
Conventional metal band	0.1	0.3
Conventional metal band, micro-etched	0.4	10
Photo-etched metal band	0.6	0.6
Photo-etched metal band, micro-etched	1.6	17

Adapted from Mennemeyer *et al*, 1999

have been compared, as well as a ceramic bracket with polycarbonate base and zirconia brackets. The bond strength of adhesive-precoated (APC) ceramic brackets (Transcend 2000, 3M Unitek) was higher than that of adhesive-precoated metal brackets. Precoating has no effect on the bond strength of the metal bracket but reduces that of the ceramic bracket. Ceramic brackets that rely on micromechanical retention and chemical adhesion for bonding of the adhesive resin to the bracket may cause cohesive enamel fractures on debonding. Ceramic brackets that rely on combined mechanical retention and chemical adhesion produce fractures located within the resin or at the bracket-resin or resin-enamel interface.

Effects of Plastic Brackets

Plastic brackets are typically polycarbonate, although some brackets are reinforced with fiberglass, glass particles or metal (Chapter 7). Bonding of an adhesive to a plastic bracket is typically mechanical and is achieved by swelling the plastic bracket base, allowing penetration of the adhesive. A plastic bracket primer such as methyl methacrylate monomer is used to cause the swelling. Utilization of the primer improves the bond strength of adhesives to plastic brackets.

Debonding of Brackets

Mechanical debonding of ceramic brackets is typically accomplished in one of three ways. The first method uses a lift-off debonding instrument (LODI). In this method, a pistol-grip plier is positioned over the bracket, and a ten-

sile debonding force is applied to the tie wings of the bracket. The second method uses a delaminating technique. Delamination occurs when a sharp-edged instrument is placed at the enamel-adhesive interface. Force application (usually with a 346 plier or cutter) produces a peeling or wedge effect to debond the bracket. The third method employs a special tool that produces a torsional or wrenching force at the base of the bracket. The delaminating method appears to be the least expensive and safest of the three methods of mechanical debonding.

Thermal debonding was developed to overcome the problems of enamel damage and high forces produced when removing ceramic brackets mechanically. When teeth are debonded with a thermal unit, bond failure is usually induced at the bracket-resin interface. Ceramic brackets that are bonded with an indirect technique typically have a resin interlayer that seems to facilitate easy removal of the brackets. A preventive approach to problems with ceramic bracket debonding is to use an indirect bonding system to place the brackets and a thermal debonding technique to remove the brackets.

A particular problem for an orthodontist is how to remove metal or ceramic brackets from teeth with a ceramic veneer without damaging the veneer. An *in vitro* study evaluated removal of ceramic and metal brackets from ceramic veneers using a Howe plier (peeling force), a lift-off debonding instrument (tensile force), and an electrothermal debonder (torquing force). The results showed that debonding of metal brackets from ceramic veneers caused some damage to the veneer regardless of the method used to remove the brackets. However, no damage to the veneer resulted

when ceramic brackets bonded to ceramic veneers were removed with an electrothermal debonding device. This study further suggested that metal brackets increase the risk of damage to the pulp when removed with an electro-

thermal debonder. The least risk to the pulp and ceramic veneer occurred when ceramic brackets were bonded to the veneer and the electrothermal debonder was used to debond the ceramic brackets.

Bonding of Brackets to Enamel – *in vivo* Studies

Chemically Cured vs. Paste-Primer vs. Light-Cured Resin Composites

In a clinical study, 37 patients had 490 metal brackets bonded with either a chemically cured resin composite (Concise) or a light-cured resin composite (Heliosit), and were followed for six months. Forty-seven brackets were lost prematurely: 37 were bonded with Heliosit and 10 with Concise. The failure rate was significantly higher for premolars than for incisors and canines with both adhesives.

A retrospective study of 548 patients with 7118 brackets bonded with a light-cured resin composite (Transbond) found an overall failure rate of 6%. The median time until bracket failure was 442 days (15 months), and there were no significant differences in time to first bracket failure with respect to the sex or age of the patient at the start of treatment. Of the 426 bracket failures, 262 failed in the upper arch and 160 failed in the lower arch. The failure rate for brackets bonded to premolars was almost twice that for brackets bonded to canines or incisors. No significant differences in bond failures were found between different operators who placed the brackets.

A paste-primer resin composite had a failure rate of 8% (6% for female patients and 11% for male patients) and a mean survival time of 46 months (48 months for female patients and 37 months for male patients) when 5941 brackets were evaluated over a five-year period. Failure rates among 14 operators varied from 5% to 12%. The failure rate for upper incisors was 5%, whereas that for premolars was 11%. More failures were associated with Begg treatment (11%) than with standard edgewise treatment (6%).

In a clinical study of 59 brackets bonded with an unfilled sealant and resin composite and 59 brackets bonded with an unfilled sealant only, there were no statistically significant differences in bond failures after six months.

A visible light-cured resin composite showed a higher failure rate (15%) clinically over six months than a chemically cured resin composite (4%). The light-cured composite appeared to be cured inadequately, particularly in the posterior region. The bond strength of light-cured resin composite can be improved by pre-curing the composite onto the bracket base. Archwires can be placed on brackets with visible-light-cured resin composites immediately after curing.

Glass-Ionomer Cements vs. Chemically Cured Resin Composites

In a prospective, three-year clinical study, 17 patients were randomly assigned to have brackets bonded with either a glass-ionomer cement (Ketac-Fil) or a resin composite (Rely-a-bond). The total numbers of bracket failures for the glass-ionomer cement and resin composite groups were 91 and 34, respectively. Based on these figures, a theoretically average patient with 20 bonded brackets would have seven bracket failures with glass-ionomer cement and three bracket failures with resin composite.

In another prospective clinical study, 60 patients had brackets bonded with a glass-ionomer cement (AquaCem) or a paste-primer resin composite (Unite). One group of patients had brackets with retentive grooves in the base (Dyna-Lock), and the other group had brackets with mesh foil base (Unitwin). The bracket failure rate was 36% with the glass-ionomer cement and 15% with the resin composite. Bracket failures for the grooved bases were 50% with the glass-ionomer cement and 23% with the resin composite. Bracket failures for the mesh bases were 22% with the glass-ionomer and 7% with the resin composite. It was noted that clean-up of enamel surfaces required less time with the glass-ionomer cement.

In a prospective clinical study, brackets for 10 patients were bonded with either a glass-ionomer cement (Fuji I) or a resin composite (System 1 +) and followed over a 12-month period. For the 60 brackets bonded, 12 failures (20%) occurred with the glass-ionomer cement compared to 3 failures (5%) for the resin composite.

In yet another prospective study, 16 patients had brackets bonded to 225 teeth, using either a glass-ionomer cement (Ketac-Cem) or a chemically cured resin composite (Concise). In a 12-month period, brackets bonded to teeth with the resin composite had an 8% failure rate, compared to a 51% failure rate for glass-ionomer cement.

Hybrid Ionomers vs. Chemically Cured Resin Composites

A new hybrid ionomer cement (Geristore) was compared to a chemically cured resin composite (Phase II) in a prospective clinical study. Forty patients had 716 brackets bonded and were followed for one year to record bond fail-

ure. The bond failure rate for the hybrid ionomer was 8.9%, compared to 3.1% for the resin composite. Additionally, it was found that the plaque around the hybrid ionomer had reduced levels of *Streptococcus mutans* and lactobacilli, compared to that around the resin composite.

In a prospective 12-month clinical study, 10 patients had brackets bonded with both a hybrid ionomer cement (Fuji II LC) and a chemically cured resin composite (System 1 +). The bracket failure rate was 3.3% in the hybrid ionomer group and 1.6% in the resin composite group.

A 3.2% bracket failure was reported in a prospective study of a hybrid ionomer (Fuji Ortho LC) used for 150 full-arch bonding cases (first molar to first molar). A control resin composite was not included in this study.

A review of clinical failure rates of orthodontic brackets bonded with glass-ionomer cements shows a failure rate that ranges from 3.2% to 50.9% over periods that range from 2.2 to 36 months. Conventional glass-ionomer cements should not be used routinely. Hybrid ionomers may be used clinically in selected cases.

Troubleshooting Bond Failures

When bond failures occur in clinical practice, the orthodontist is faced with the potentially bewildering problem of determining the causes of these failures. Tables 5.12 and 5.13 provide

practical lists of the possible causes of adhesive-enamel and adhesive-bracket bond failures, respectively.

Table 5.12 Possible causes of adhesive-enamel bond failures (adhesive left on bracket, little left on tooth)

- Contamination of the etched enamel by saliva, moisture or oil from water line
- Insufficient rinsing of etchant from tooth before bonding
- Inadequate drying of enamel surface precludes penetration of resin
- Over-etching demineralizes enamel, reduces depth of resin tags penetration, and removes excessive amounts of enamel
- Faulty bonding materials are unlikely, but expiration dates should be checked and care taken in handling of materials
- No activator was placed on enamel surface when a no-mix adhesive was used
- Tooth surface required special preparation because of amalgam, gold, ceramic, or other restorative material

Table 5.13 Possible causes of adhesive-bracket bond failures (adhesive left on tooth, little left on bracket)

- Excessive force exerted on bracket from occlusion or excessive force from appliance
- Movement of bracket during initial setting of adhesive
- Contaminated bracket mesh (oil from hands, glove powder, or rebonded bracket)
- Adhesive not "battered" into base firmly
- Activator not placed on bracket in paste-primer system
- Inadequate cure of light-cured resin composite (output of light-curing unit should be checked)
- Special primer required (plastic brackets)

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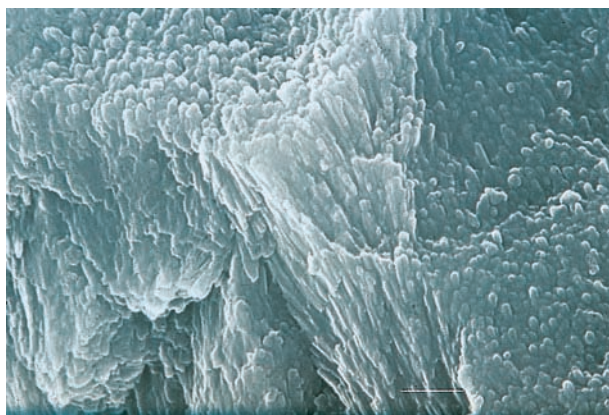
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6 Oral Microbiological Changes, Long-Term Enamel Alterations Due to Decalcification, and Caries Prophylactic Aspects

Bjørn Øgaard



SEM micrograph of an initial caries lesion about 50 μm beneath the surface. Scale bar length = 1 μm

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Introduction

Advances in diagnostic methods and treatment techniques during the past decades have provided orthodontists with tools capable of giving their patients improved aesthetic facial appearance, well-functioning occlusion, and knowledge to maintain their dentition in good condition. Modern appliance design and techniques transmit light forces to teeth and the surrounding structures that minimize the potential risk of adverse effects during treatment. Nevertheless, side effects do occur as a result of orthodontic therapy. Some of these effects are caused by the appliance (e.g., caries, gingival inflammation, marginal bone loss, and allergic reactions) and others by the forces applied (e.g., pulp necroses and root resorption). Clearly, it is the responsibility of the orthodontist to be aware of these risks and take precautions to avoid or limit their development.

Enamel decalcification and lesion formation are major clinical problems for patients treated with fixed orthodontic appliances (Fig. 6.1). To be able to diagnose and prevent caries dur-



Fig. 6.1 Severe decalcifications on the upper anterior teeth after treatment with fixed orthodontic appliances

ing fixed appliance therapy, the orthodontist must be familiar with all aspects of the caries process and topical fluoride application. The present chapter reviews the most recent findings in caries and fluoride research, and relates these findings to orthodontic treatment with fixed appliances.

Oral Microbiological Changes

Individuals with malocclusions often have many retention sites owing to the irregularities of their teeth. More retention sites are introduced when orthodontic appliances are bonded or banded to the teeth. Oral hygiene is thus markedly more difficult to carry out for orthodontic patients than for individuals with normal dentition. Gwinnett and Ceen showed that fixed orthodontic appliances induce a rapid increase in the volume of dental plaque. Chatterjee and Kleinberg subsequently reported that the plaque in orthodontic patients had a resting pH lower than that in non-orthodontic subjects. The plaque-retentive properties of the appliance thus result in a severe cariogenic challenge on the labial surfaces where caries usually does not develop. This may explain the much stronger relationship between oral hygiene and caries incidence in orthodontic patients than in non-treated individuals. The increased amount of plaque in association with orthodontic appliances also rapidly induces gingival inflammation,

especially in relation to bands (Fig. 6.2). This gingival inflammation is thought to be due to unspecific bacteria in plaque and is usually reversed after debonding and debanding.

There is a rapid shift in the bacterial flora of plaque after introduction of orthodontic appliances. Unlike gingival inflammation, caries is



Fig. 6.2 Plaque accumulation and gingivitis in a patient under treatment with fixed orthodontic appliances

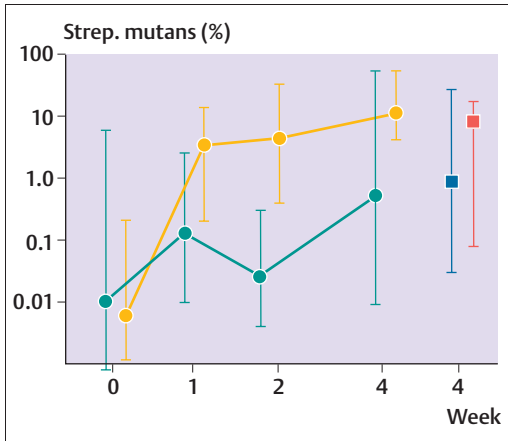


Fig. 6.3 Median changes in *S. mutans* in plaque behind specially designed orthodontic bands (gold circles) and on non-banded surfaces (green circles). Note the logarithmic scale. (Modified from Arneberg *et al*, 1984)

associated with acidogenic bacteria. Experiments using specially designed orthodontic bands showed an exponential increase in the number of *Streptococcus mutans* (*S. mutans*) and lactobacilli in the plaque behind the bands (Fig. 6.3). Scheie and co-workers observed significantly elevated plaque and salivary levels of *S. mutans* after insertion of orthodontic appliances. Both *S. mutans* and lactobacilli are often associated with caries development. They are aciduric bacteria and produce organic acids in the presence of fermentable carbohydrates. Sucrose plays a particular role in plaque formation, inducing the formation of a cariogenic plaque. Lactobacilli are generally associated with progression of caries lesions. High levels of *S. mutans* and lactobacilli in plaque indicate an increased risk of caries. Table 6.1 shows the long-term development of *S. mutans* (logarithm to base 10 of total numbers) and the percentage of *S. mutans* in plaque during orthodontic treatment with fixed appliances. The data demonstrate a rapid increase of the total number and the percentage of *S. mutans* in plaque of orthodontic patients during the entire treatment period, and thus the maintenance of a potentially highly cariogenic environment in the plaque around the appliances. However, the association between caries and bacteria is not a simple one. Several recent studies have shown that prediction of caries

development based on bacterial counts is uncertain and of little clinical significance.

Arneberg *et al* studied the pH of plaque in orthodontic patients following a sucrose challenge. By using a microtouch electrode, it was possible to monitor pH changes at different individual sites of the dentition rather than use pooled plaque samples. The lowest pH during resting and fermenting conditions was observed in the plaque of the bonded upper incisors. In these sites, the pH could fall as low as 4. The low pH in the upper anterior region is most likely due to the slow salivary clearance at this location, allowing prolonged retention of acids in the plaque. Interestingly, total plaque fluoride levels were also lowest at these sites, suggesting a direct relationship between plaque pH and total plaque fluoride. It is speculated that the low fluoride concentration in plaque of the bonded anterior teeth is due to increased release of fluoride at low pH.

Eliades *et al* have studied the wettability and early pellicle formation on different bracket materials, as described in Chapter 1. The bracket materials are discussed at length in Chapter 7. Stainless steel presented the highest critical surface tension, and polycarbonate and alumina materials the lowest. It was speculated that this could result in reduced plaque-retaining capacity of polycarbonate and alumina brackets relative to stainless steel appliances. Fournier *et al* reached the opposite conclusion from an *in vitro* study, where metal brackets presented a lower potential for bacterial accumulation than plastic and

Table 6.1. The average logarithm of the number and the percentage of *S. mutans* in the plaque of 114 patients with fixed orthodontic appliances, followed longitudinally for the entire treatment period

Condition Period	log ₁₀ <i>S. mutans</i> in Plaque ^a	Percent <i>S. mutans</i> in Plaque
Bonding	2.4	0.1
12 weeks	3.5	1.5
24 weeks	3.8	1.1
72 weeks	4.1	2.0
Debonding	4.2	1.7

^a Logarithm of total number.

ceramic brackets. The presence of saliva, however, lowered the adherence of *S. mutans* to brackets of all the materials. The clinical sig-

nificance of these observations is unclear, and additional research under *in vivo* conditions is necessary.

Long-Term Enamel Alterations Due to Decalcification

Dental caries involves dissolution of tooth mineral due to organic acids produced by plaque bacteria. To understand the dynamics in the caries process, it is necessary to know the characteristics of sound enamel and the biological and physiochemical events taking place during enamel dissolution. Knowledge about the caries rate in general and for orthodontic patients in particular, and of the mechanism of action of fluoride, is essential to design a caries prophylactic program suitable for the individual orthodontic patient.

Sound Enamel

Enamel is characterized by a high mineral content (96 wt%) and by a low content of organic matter (0.4–0.8 wt%) and water (3.2–3.6 wt%). The mineral phase is generally described as calcium hydroxyapatite, which belongs to an isomorphous series of compounds known as apatites. The tightly packed, hexagonal, needle-shaped crystallites of the

hydroxyapatite are the real units of enamel and are arranged into prisms. The appearance of the “keyhole”-shaped prisms radiating from the dentin-enamel junction toward the outer surface is due to differences in the orientation of the crystallites (Fig. 6.4). In the interprismatic area, the crystallites are more randomly oriented and loosely packed, and consequently this area contains more water and organic matter than within the prisms. Firmly bound water is mainly present as hydration shells around the crystallites.

The enamel is extremely heterogeneous from a chemical point of view, and it has been shown that a large number of impurities are present in enamel, particularly in the caries-susceptible areas. Sodium, carbonate, and fluoride ions may exchange for calcium, phosphate, and hydroxyl ions, respectively. The apatite in enamel is non-stoichiometric, probably owing

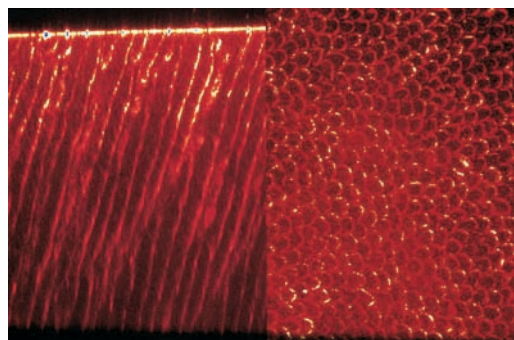


Fig. 6.4 Confocal laser scanning microscopic image of sound enamel. The interprismatic enamel appears as light colors, and the prism centers as dark colors. Note the typical keyhole or honeycomb structure of the prisms. **Left:** Optical section perpendicular to the surface. **Right:** Optical section parallel to the surface. (Courtesy of Professor Heinz Duschner, University of Mainz, Germany)



Fig. 6.5 Scanning electron microscope (SEM) micrograph of sound enamel from a newly erupted premolar. Note the typical perikymata pattern

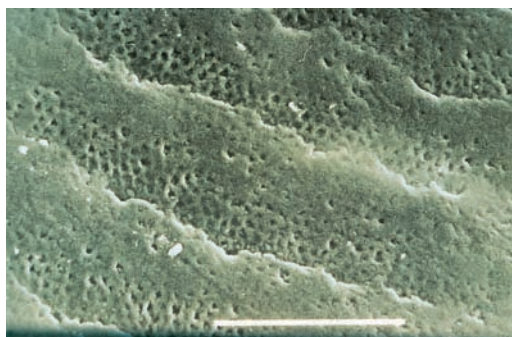


Fig. 6.6 Initial caries development along the perikymata lines. Note the opening of the prism endings. Scale bar length = 20 μm . (From Arends *et al*, 1987)

to calcium deficiencies and the presence of the sodium and carbonate ions. More carbonate ions are found in deciduous enamel than in permanent enamel, which may be one factor why lesion progression in deciduous enamel is faster than in permanent enamel. Surface enamel is harder, and tends to have higher mineral content and lower water content than subsurface enamel. In addition, several ionic species with high affinity for the mineral phase (e.g., fluoride, zinc and lead) are present in higher concentration in surface enamel.

In the scanning electron microscope (SEM), surface enamel exhibits large variation, probably due to age and site in the oral cavity. Macroscopically, and in the SEM, surface enamel of newly erupted teeth exhibits the so-called

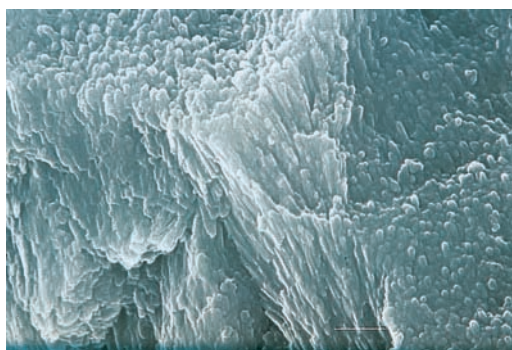


Fig. 6.7 SEM micrograph of an initial caries lesion about 50 μm beneath the surface. Note the increased porosity along the interprismatic areas and the dissolution of single crystals. Scale bar length = 1 μm . (From Arends *et al*, 1987)

perikymata or imbrication lines (Fig. 6.5). It has been found that perikymata geometrically represent closed circles. Subsequent to tooth eruption, the perikymata are progressively worn away over the years as a result of normal function and toothbrushing. Perikymata are thus rare in adults. Also, the bonding and debonding procedures of orthodontic brackets contribute to loss of the perikymata. Studies using orthodontic bands to induce plaque on premolars to be extracted for orthodontic treatment have shown that the initial caries process starts along the perikymata lines by exposing the prism endings (Fig. 6.6) and then progressing along the interprismatic areas (Fig. 6.7).

The Early Enamel Caries Process – the White Spot Lesion

It is the tight packing of the crystals that makes enamel translucent. Increase in the porosity of the enamel leads to changes in the optical properties, as light is scattered. The white appearance of early caries lesions is thus an optical phenomenon. The whiteness increases when the white spots are dried by air, since water is replaced by air, and air has a lower refractive index than hydroxyapatite and water. The lesion area is slightly softer than the surrounding sound enamel.

Three types of enamel lesions may develop, depending upon pH and fluoride concentration in the plaque fluid (Fig. 6.8). When pH drops below the critical pH of enamel (~ 5.5), plaque fluid becomes undersaturated with respect to hydroxyapatite, and the enamel starts to dissolve. Using orthodontic bands on a pair of pre-

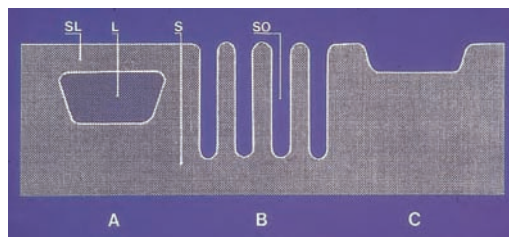


Fig. 6.8 Schematic drawing of the three types of lesions that may develop in enamel depending on the pH in plaque fluid: A, subsurface lesion; B, surface softened lesion; C, erosion. (SL = surface layer; L = lesion body; SO = surface softening)

molars to be extracted as part of fixed appliance therapy, it was possible to monitor the caries process from week to week. Clearly, the initial enamel lesion causes softening of the surface. This softening is characterized by a gradual decrease of the mineral content in the surface enamel, caused by preferential dissolution of interprismatic mineral. On microradiographs, these lesions lack a surface layer. The typical subsurface lesion with a porous surface layer is formed later in the caries process and requires that plaque fluid becomes supersaturated with respect to fluorapatite. Thus, in the presence of fluoride, the critical pH of enamel is lowered from 5.5. to 4.5. When the pH of plaque fluid is lower than ~ 4.5 , plaque is still undersaturated with respect to hydroxyapatite and also to fluorapatite, and an erosion is formed. This is also where there is a limitation for the cariostatic effect of fluoride (see below).

The General Caries Situation

During recent decades, the prevalence of dental caries in school children has decreased by more than 70% in Western Europe and in the United States. In the United States and the Nordic countries, 50% of 12-year-old and more than 70% of the 5-year-old children are caries-free. Very few 18 to 19-year-old adults are caries-free, but the average DMFT (decayed/missing/filled teeth) index is less than 6, with mainly posterior lesions and fillings. In those countries where caries has declined, it is interesting to note that not only has the prevalence of caries changed but also the distribution of lesions in the dentition; lesions on smooth surfaces occur less often. Caries is increasingly becoming a pit and fissure phenomenon. Furthermore, already established lesions progress more slowly than earlier.

It is important to note that caries is not a disease limited to children. As many as 95% of adults have experienced caries, showing that people are at risk of caries throughout life. In Eastern Europe dental caries is still a significant problem, and caries prevalence is reported to increase in some developing countries, presumably owing to increased sucrose consumption.

Average data do not necessarily give a true picture of the caries distribution in the popula-

tion. While almost all individuals had a high caries rate in the past, in some countries 20% of the 12-year-olds now account for 80% of all clinical caries lesions. In the Nordic countries, only those lesions that require restorative therapy are formally recorded as caries; *i.e.*, the DMFT/S indices are mainly applicable to caries that has progressed into dentin. A significant number of initial enamel lesions in the proximal surfaces have been observed in 18-year-olds, but these are not included in the statistics. It has been speculated that these lesions may in time develop into dentinal lesions. In this way the actual caries prevalence in the population could be masked, and a more favorable picture would be presented than was justified. However, cross-sectional studies in 35-year-olds in Oslo in 1973, 1984, and 1993 have clearly shown a reduced caries prevalence in the adult population, also. The caries reduction observed among children and adolescents thus seems to be maintained as a permanent reduction in caries prevalence into adulthood.

Orthodontic Treatment and Caries Development

Orthodontic treatment is generally carried out during childhood and adolescence. This is a period when caries incidence is relatively high. Because of visual obstruction by the appliance, development and progression of lesions in the proximal surfaces may be difficult to diagnose. Bands protect the proximal surfaces (Fig. 6.9). The appliance may also make X-ray examination more difficult.

A number of studies have investigated the relationship between orthodontic treatment with fixed appliances and caries development. Some previous studies showed increased caries frequency in subjects receiving orthodontic treatment, whereas more recent investigations did not confirm such correlation. Zachrisson and Zachrisson reported that orthodontic treatment with banded appliances did not increase the prevalence of dental caries. However, in orthodontically treated individuals, they observed a shift in the distribution of lesions from posterior to anterior teeth and from interproximal to facial/lingual surfaces. The bands obviously protected the proximal surfaces from dissolution. The gap between the band

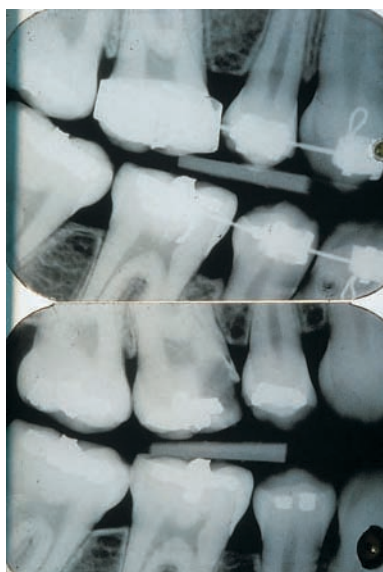


Fig. 6.9 Large caries lesion on upper first molar detectable only after debanding. Note that the archwire in the lower dentition masks the proximal surfaces

and the gingival margin on the labial surface of the anterior teeth, on the other hand, resulted in plaque accumulation and the development of lesions.

During recent decades, along with the marked decline in caries in the population, orthodontic treatment techniques have changed from banded to mainly bonded appliances. Today bands are used mainly on the molars. The protection given by bands on proximal surfaces of the incisors and premolars is no

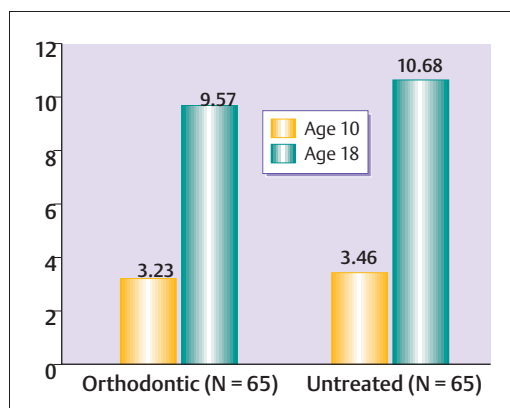
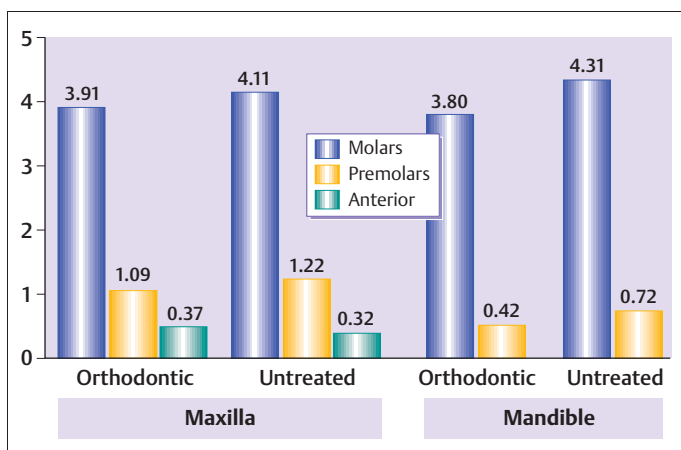


Fig. 6.10 Mean number of filled surfaces (FS) at the ages of 10 and 18 in orthodontically treated patients and non-treated individuals. (From Øgaard, 1989a)

longer present. The incidence of filled teeth from 10 to 18 years of age has been evaluated in individuals treated with mainly bonded orthodontic appliances. The mean age at the start of treatment was 12 years, and the mean treatment time was two years. A group who had not received orthodontic treatment served as the control. The study showed no significant differences in filled surfaces between the orthodontic group and the untreated group at the age of 10 years, approximately two years prior to treatment, and no significant difference several years after treatment at the age of 18 years (Fig. 6.10).

The distribution of restorations in the dentition did not show any significant difference at the age of 18 years (Fig. 6.11). It has

Fig. 6.11 Distribution of restorations in molars, premolars and anterior teeth at the age of 18 in orthodontically treated and non-treated individuals. (From Øgaard, 1989a)



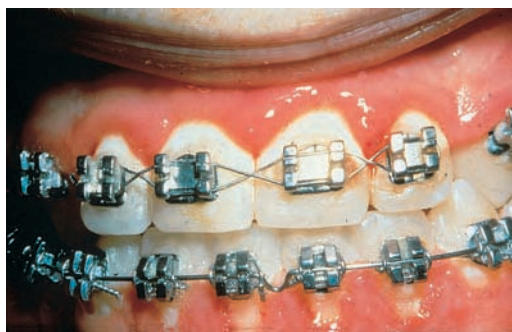


Fig. 6.12 Severe white spot lesions developed along the gingival margin during treatment with fixed orthodontic appliances



Fig. 6.13 Thin white spot lesion present along the gingival margin on the upper lateral incisor at debonding

been argued that a substantial number of incipient enamel lesions could have formed during orthodontic treatment and that these subsequently become deep lesions after treatment was concluded. However, this study recorded filled surfaces about five years after treatment, which is probably more than the average time for progression of caries in the enamel. From the previous discussion, it seems that a caries lesion developed during orthodontic treatment would be restricted to the outer enamel surface and would not necessarily progress when fluoride toothpaste was used regularly.

Several reports have shown an increased incidence of early enamel caries (white spot lesions) on the labial enamel surface during orthodontic treatment (Figure 6.12). These white spot lesions rarely progress into becom-

ing significant cavities and are generally not registered as caries requiring filling therapy in the DMFT/S indices. Gorelick and co-workers observed that as many as 50% of subjects experienced an increase in the number of white spot lesions with fixed orthodontic appliances when no preventive fluoride programs were used. Usually the first molars and upper lateral incisors are most affected (Fig. 6.13). Even with regular use of a fluoride dentifrice, enamel dissolution may occur around orthodontic brackets. Using specially designed orthodontic bands, visible white spot lesions could be induced within four weeks, *i.e.*, within the period between one clinical appointment and the next. Initial caries developed in the cariogenic environment of an orthodontic appliance may thus become a rapidly progressing process.

Caries-Prophylactic Aspects of Orthodontic Treatment

Importance of Fluoride for Decline of Caries

There is reason to believe that the decline in caries prevalence in children and adolescents in the industrialized countries during the last few decades can be ascribed almost exclusively to the increased use of topical fluoride, mainly as fluoride toothpastes. Hardly any other factor can explain this phenomenon. Caries reduction coincides with the introduction of fluoride toothpaste in most countries. The market penetration achieved by fluoride dentifrices since

1960 has grown to more than 90% in most industrialized countries. On a global basis, this phenomenon has made toothpaste a more important fluoride vehicle than public drinking water. Unlike water fluoridation, which is a passive form of caries prevention, the use of fluoride dentifrice requires active participation by the individual if it is to have any effect. To estimate the preventive potential of fluoride dentifrices, Ronis and co-workers analyzed toothbrushing patterns along with common sociodemographic variables. The data indicated a near-universal acceptance of toothbrushing as a daily personal health habit.

There are no indications that diet, oral hygiene, or virulence of the plaque bacteria have changed in such a way that one or more of these factors could have influenced caries development in the population. In contrast, the consumption of sweets and sugar-containing soft drinks has increased enormously in the industrialized countries. These factors should be taken into consideration when caries prophylactic-programs are planned.

Cariostatic Mechanism of Fluoride

Fluoride is the most cariostatic agent known, and its mechanism of action is complex. Originally, fluoride given during tooth formation (systemic fluoride) was thought to induce formation of a fluoride-containing enamel that was less susceptible to dissolution by organic acids produced in plaque. Very little fluoride is in fact incorporated into enamel through the use of systemic fluoride. This incorporated fluoride is located superficially in the enamel and is lost by wear during the first years after eruption. A newer concept suggested by Driessens is that fluoride serves as a catalyst during tooth formation. Thus, fluoride improves the quality of mineralized tooth tissues in general by reducing the relative amounts of carbonate apatite and magnesium whitlockite, which are softer and more soluble in acid than is hydroxyapatite. However, no clinical data have proved this concept. The systemic effect of fluoride is probably less important than the topical effect. It is now generally believed that the major cariostatic mechanism of fluoride is due to its effect in plaque fluid around the mineral crystallites, by inhibiting demineralization and increasing remineralization of mineral lost during the caries process (Fig. 6.14).

During topical fluoride application, an intermediate reservoir of fluoride is formed on the surface, in initial lesions, and in plaque. This material is visible in the scanning electron microscope as small globules ($< 1 \mu\text{m}$) on the surfaces of fluoride-treated teeth, and has been shown to contain mainly calcium and fluoride (Fig. 6.15). Since pure calcium fluoride would have a cubic external morphology, rather than spherical, and the globules consist of microcrystals, the material is described as calcium

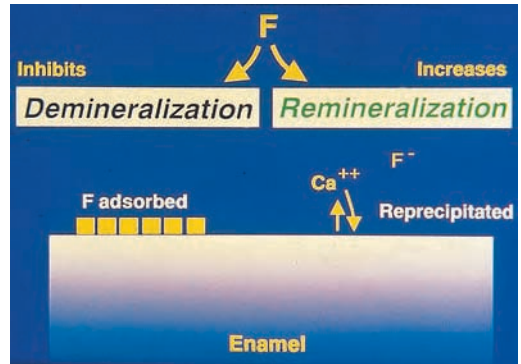


Fig. 6.14 Schematic illustration of the effect of fluoride in plaque fluid on the demineralizing and remineralizing processes

fluoride-like. These globules are soluble in alkali solutions and contain traces of phosphate ions; accordingly, the terms alkali-soluble fluoride and phosphate-contaminated fluoride are also used to describe the globules. The amount and size of the globules depend on the pH, the concentration of the fluoride solution, and the exposure time. The globules appear to form preferentially in prism depressions and focal holes along the perikymata grooves, which are more soluble than other parts of the enamel.

Calcium fluoride is soluble in water (15 mg/L), and its solubility in saliva was previously supposed to be identical to that in water. This was based on theoretical calculations rather than on experiments. Some clinical

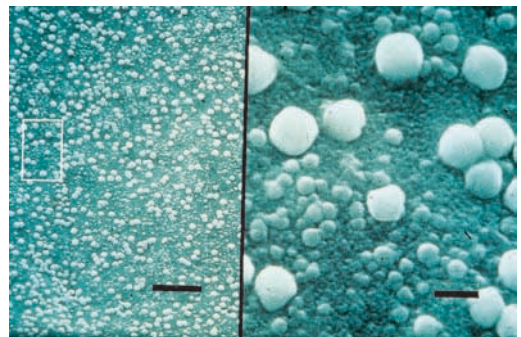


Fig. 6.15 Scanning electron microscope image of calcium fluoride globules induced by treating enamel with a neutral 2% sodium fluoride solution. **Left:** Scale bar length = 10 μm . **Right:** Scale bar length = 1 μm

studies indicated that the calcium fluoride formed was lost in 24 hours, when it was subsequently exposed to the oral environment. However, more recent investigations in several laboratories have shown that calcium fluoride is quite insoluble in saliva at neutral pH, and that the calcium fluoride can persist on the tooth surface for weeks and months after topical application of fluoride. It is now believed that calcium fluoride is the *only* phase that forms during brief topical fluoride application.

The reason for the prolonged retention of calcium fluoride on the enamel is the coating of the calcium fluoride at neutral pH by secondary phosphate (HPO_4^{2-}) ions and possibly by proteins, as shown schematically in Figure 6.16a. At lower pH, such as during a caries attack, the phosphate ions mainly change to primary phosphate ions (H_2PO_4^-), which do not block the surface. Thus, fluoride and calcium ions are released at low pH, as illustrated in Figure 6.16b. The fluoride ions adsorb to the enamel crystals and stabilize the enamel against dissolution. The fluoride ions also enhance remineralization. After the caries attack, the pH increases, and Figure 6.16c shows that the calcium fluoride globules are again stabilized by secondary phosphate ions and proteins. Calcium fluoride is thus a reservoir of fluoride ions. The potential for formation of calcium fluoride should probably be increased in preparations designed for the topical application of fluoride, and not reduced or eliminated as was believed in the past.

The limit of the fluoride effect is reached when pH drops so low that even the solubility product of pure fluorapatite is not exceeded (Fig. 6.17). This pH is presumably below 4.5. It has been shown that bacteria associated with caries (*S. mutans* and lactobacilli) may lower the pH in dental plaque below 4.5. At this low pH the liquid phase of the plaque will be undersaturated with respect to both hydroxyapatite and fluorapatite, and no redeposition of lost mineral (remineralization) will occur. This is most important for the clinical situation. In old, acidic plaque more fluoride will not necessarily give further protection against lesion progression due to the low pH. This may be one reason for the observation that fissure caries has shown the lowest reduction in recent decades and that lesions may rapidly develop underneath poorly-fitting bands and around

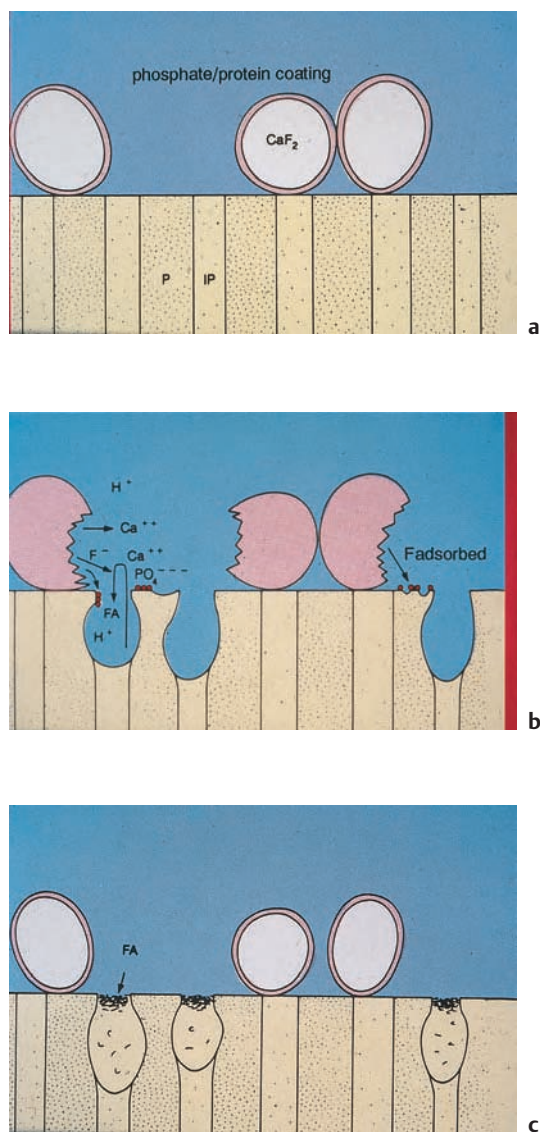
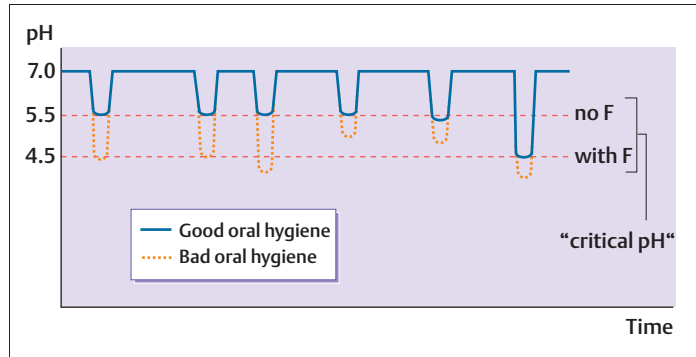


Fig. 6.16 (a) Globules of calcium fluoride-like materials on the enamel surface after topical fluoride treatment. A coating of secondary phosphate ions and proteins stabilizes the globules at neutral pH. (b) During a caries attack, the pH is lowered and the dissolution rate of the calcium fluoride material is increased. The released fluoride increases the rate of remineralization and inhibits demineralization. (c) After the caries attack, the pH neutralizes and the phosphate ions and proteins protect the remaining calcium fluoride-like material. The caries lesions are repaired, and the fluoride concentration is increased in the enamel

Fig. 6.17 The Stephan curve showing the effect of fluoride on the critical pH at which demineralization occurs. Fluoride lowers the critical pH from 5.5 to 4.5



orthodontic brackets, even when fluoride is used regularly. Under such conditions a dose-response effect to fluoride may not be apparent, e.g., more fluoride may not give a better clinical effect.

It has been shown that the “calcium fluoride” formed on tooth surfaces upon topical application of fluoride contains phosphate ions, not only on the surface, but also inside the crystal. This phosphate-contaminated calcium fluoride is more soluble than pure calcium fluoride and may thus release fluoride at a higher rate than the pure substance. The amounts of phosphate ion incorporated into the calcium fluoride crystals are dependent on the conditions under

which they were formed. Calcium fluoride formed on tooth surfaces at high concentrations of fluoride or at low pH contains less internal phosphate and is less soluble than calcium fluoride formed under other conditions. This gives the opportunity in the future to induce formation of tailor-made fluoride reservoirs on the teeth. A long-lasting, resistant layer of calcium fluoride could be beneficial for topical application performed at three-month or six-month intervals. A more soluble calcium fluoride may be more suitable in preparations that are used frequently, for example, in toothpastes.

Rational Caries Prophylactic Measures for Orthodontic Patients

It is logical to differentiate between the prevention of caries lesion development during orthodontic treatment and the treatment of lesions present on labial surfaces at debonding. Since fluoride is the most important agent in caries prevention, the greatest emphasis will be given to different forms of fluoride prophylaxis.

Prevention of Caries Lesion Development during Orthodontic Treatment

Fluoride Toothpastes

Fluoride toothpaste is the basis for all caries prevention. Most toothpastes contain sodium fluoride, monofluorophosphate, stannous fluoride, or amine fluoride. The fluoride concentra-

tions may vary, but the maximum concentration allowed in the European Community is 0.15%. A dose-response effect to fluoride toothpastes has been demonstrated, and fluoride concentrations below 0.1% should not be recommended for orthodontic patients.

The cariostatic potential of fluoride toothpastes is most likely larger than generally shown in clinical studies. This is due to a cumulative effect of fluoride through remineralization as a function of time. Furthermore, the cariostatic effect will improve significantly if oral hygiene is also improved, as discussed previously. Good oral hygiene is thus more important in orthodontic patients treated with fixed appliances than in non-treated individuals.

Stannous fluoride has a plaque-inhibiting effect in addition to an anticaries effect. The stan-

nous ion rather than the fluoride ion is responsible for the plaque-inhibiting effect. Stannous ions interfere with the adsorption of plaque bacteria to enamel by being bound to the phosphate polymer lipoteichoic acid present on the surface of Gram-positive bacteria. Stannous fluoride also interferes with the acidogenicity of plaque. It is possible that tin atoms bound to the surfaces of the bacteria also block the passage of sucrose into the cell and inhibit acid formation. Stannous fluoride may therefore offer beneficial effects not only against caries but also against plaque-induced gingival diseases during orthodontic treatment.

Detergents are surface-active agents and are incorporated into toothpastes and mouthrinses to lower the surface tension of the fluid environment in the mouth, to penetrate and loosen surface deposits on the teeth, and to emulsify and suspend the debris that is removed from the tooth surfaces. Detergents are responsible for the foaming properties and the taste of toothpastes, and thus they play a major role in the acceptance of toothpastes by consumers. Detergents also exhibit antimicrobial activity, owing to their interference with membrane structures and various biological processes in microorganisms. The anionic agent sodium lauryl sulfate (SLS) is the most popular detergent in toothpastes. It has, however, been shown that the permeability of the oral mucosa is increased in the presence of SLS. Exposure of the oral mucosa to SLS may therefore potentiate the effect of allergens. Guinea-pigs became sensitized to nickel and chromium ions only when these agents were mixed with SLS. In patients with allergic stomatitis, who were sensitized to various food proteins, a significant decrease in the amount of oral ulcers was reported when SLS-containing toothpaste was avoided. The ulcerogenic effect of SLS was due to its denaturing influence on glycoproteins in the oral mucin layer, inducing an increased mucosal exposure to food proteins. Toothpastes without SLS may therefore be a good alternative in orthodontic patients experiencing ulcers from the appliance, who are potentially allergic to nickel and chromium, or who suffer from recurrent aphthous ulcers.

Fluoride Supplements

For the average orthodontic patient, O'Reilly and Featherstone found that toothpastes were unable to stop the development of lesions. Orthodontic patients are therefore requested to use a fluoride mouthrinse (0.05 % NaF) daily, in addition to fluoride toothpaste. Experimentally, it has been shown that conventional fluoride mouthrinses reduce lesion development significantly underneath bands, though no complete inhibition is obtained if the cariogenic challenge is severe. An improved cariostatic effect of fluoride mouthrinses has been obtained by combining fluoride with antibacterial agents like chlorhexidine, triclosan, and zinc. Chlorhexidine inhibits plaque formation, although its long-term clinical applicability is somewhat limited by discoloration of the teeth and tongue and a metallic taste. Triclosan has an antibacterial effect and is often combined with zinc to increase the antiplaque effect of zinc. Furthermore, triclosan has an anti-inflammatory effect. The addition of triclosan to SLS reduced pain and desquamation caused by exposure to this agent. The new fluoride mouthwashes containing triclosan may therefore offer potential benefits for orthodontic patients.

Fluoride mouthrinsing is dependent on cooperation by the patients. Geiger and co-workers showed that less than 15 % of the orthodontic patients rinsed daily with fluoride as requested. Since fixed orthodontic appliances introduce such a high and long-lasting cariogenic challenge, there is a need for more continuous fluoride supplementation independent of patient cooperation. Therefore, some topical fluoride in the form of varnishes, solutions or gels may be recommended. There is no distinct difference in the caries-preventive effect of these concentrated fluoride agents; thus, the choice of method depends on cost, convenience, patient acceptance, and safety. The use of fluoride varnishes has proved to be a feasible and safe method of fluoride application. With fluoride varnishes the amounts of fluoride exposure can be better controlled, and less chair-time is required, compared with conventional solutions and gels. No dose-response effect to concentrated fluoride agents is apparent, and the benefit of frequent application is not clearly established. If caries activity remains high in spite of regular use of toothpaste and

topical fluoride applications, additional methods of caries prevention with the aim of reducing the challenge (improved oral hygiene, antimicrobials, and other agents that deposit acid-resistant coatings) should be applied instead of increasing the level of fluoride exposure.

Several attempts have been made to enhance the cariostatic potential of current fluoride agents and procedures for orthodontic purposes. An improved cariostatic effect of topical fluoride was demonstrated in an orthodontic appliance model of a fluoride solution with low pH. If a continuous layer of small particles containing calcium fluoride covers the enamel completely, this layer can protect the enamel to a higher degree than fluorapatite, because the solubility of calcium fluoride is less pH-dependent than that of fluorapatite, as shown in Figures 6.18a and b. Calcium fluoride formed at low pH is also less soluble than calcium fluoride formed at neutral pH, since phosphate ions do not interfere with its formation. Acidic fluoride agents without addition of phosphate ions give better clinical effects under severe cariogenic challenges than do presently available fluoride agents.

Solutions of titanium tetrafluoride inhibit lesion development in association with fixed orthodontic appliances markedly more efficiently than is possible with conventional preparations. The cariostatic mechanism of titanium tetrafluoride is probably due to the retentive, titanium-rich, glaze-like coating formed on treated enamel surfaces. At low pH, titanium binds with an oxygen atom of a phosphate group, which is densely distributed on enamel surfaces. Following the application of aqueous solutions of titanium tetrafluoride, $-Ti-O-Ti-O-$ chains are formed on the tooth surface, and covalently bound titanium atoms cover this surface. A strong complex is thus formed between the titanium compounds and the hydroxyapatite. This surface coating has been found to resist challenges even under extreme alkaline and acidic conditions. Titanium tetrafluoride is probably the only fluoride compound for which the cariostatic effect is not due to the fluoride ion. The fluoride ions are firmly bound to titanium at low pH and are only released by being exchanged with hydroxyl ions at high pH.

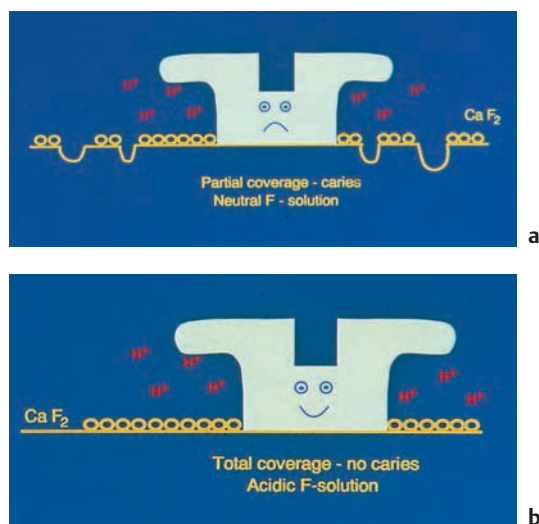


Fig. 6.18 (a) Severe cariogenic challenge adjacent to an orthodontic bracket. Partial protection against demineralization is provided by a scattered layer of calcium fluoride-like material induced during topical treatment with a neutral fluoride agent. (b) Severe cariogenic challenge adjacent to an orthodontic bracket. Total protection against demineralization is provided by a complete acid-resistant layer of either calcium fluoride-like material or titanium tetrafluoride

Fluoride-Releasing Bonding Agents

Fluoride-releasing bonding agents have attracted much interest, since they provide a fluoride reservoir that does not depend on patient cooperation. Furthermore, fluoride is deposited directly to the caries-susceptible sites adjacent to the brackets and bands. Fluoride-releasing adhesives, glass-ionomer cements, and resin-reinforced glass-ionomer cements have been introduced for orthodontic purposes. The glass-ionomer cements are discussed in Chapter 11. Bonding of brackets with resin composites requires pretreatment of the enamel with phosphoric acid, and hence minerals are necessarily lost. The glass-ionomer cements are of particular interest since no acid etching is required.

Glass-ionomer cements bond to enamel chemically through calcium bridges, hydrogen bonds, or van der Waals forces (Chapter 11). In this way glass-ionomer cements provide a stronger bond and are not as easily washed out as conventional cements. However, when

used as bonding agents for brackets, glass-ionomer cements are clearly weaker than resin composites (Chapter 5). Light-activated glass-ionomer cements are faster-setting and have shown higher initial and sustained shear bond strengths than chemically cured glass-ionomer cements. For long-term use, a higher failure rate may thus be expected when brackets are bonded with glass-ionomer cements than when conventional resin composite adhesives are used. This appears to be mainly due to poor cohesive properties rather than to the adhesive properties.

Resin-reinforced glass-ionomer cements have shown higher tensile bond strengths and lower failure rates than chemically cured glass-ionomers. Resin-reinforced glass ionomers are light-cured cements, and this results in an increase in the amount of material that undergoes setting. The resin-modified glass-ionomer cements contain components present in both conventional glass-ionomers and resin composites, and set both through an acid-base reaction and through polymerization (Chapter 11). These hybrid-type products release at least as much fluoride *in vitro* as do conventional glass-ionomer cements. Photo-

polymerizable monomers and hydroxyethyl methacrylate (HEMA) have also been incorporated into resin-reinforced glass-ionomer cements. The setting chemistry of resin-modified glass-ionomer cements is complex and differs from that of conventional glass ionomers.

In studies simulating oral conditions, it was found that fluoride availability from glass-ionomer cements is pH-controlled, e.g., fluoride release is increased as the pH in plaque decreases (Fig. 6.19). The rate-controlling factors appear to be the concentrations of the phosphate ions and proteins. Data for fluoride release in water may therefore underestimate the long-term effects. Glass-ionomer cements may also take up fluoride from topical treatment. It has been speculated that calcium fluoride may form during "recharging" of glass-ionomer cements with fluoride, acting as a reservoir of fluoride for release during cariogenic challenge.

Short-term clinical experiments involving bonding of brackets with glass-ionomer cements have shown that fluoride release significantly inhibits lesion formation, compared to a nonfluoride adhesive. However, clear evidence of erosion adjacent to the brackets supports the hypothesis that the cariostatic effect of fluoride is limited in some situations (Fig. 6.20).

Resin composites used for bracket bonding may also release fluoride ions. Fluoride can be

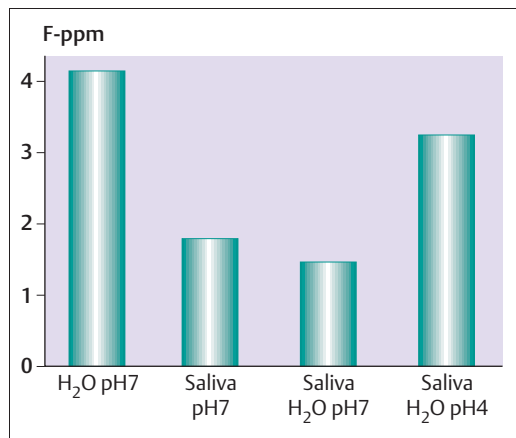


Fig. 6.19 Dissolution of a glass-ionomer cement in water for one hour at pH 7, in saliva, in water at pH 7 after precoating with saliva, and in water at pH 4.5 after precoating with saliva. The dissolution in saliva is slower than in water. Precoating of the glass-ionomer cement with saliva also reduces the dissolution. Lowering the pH in water increases the dissolution when the glass-ionomer cement is precoated with saliva. (From Rezk-Lega *et al*, 1991b)

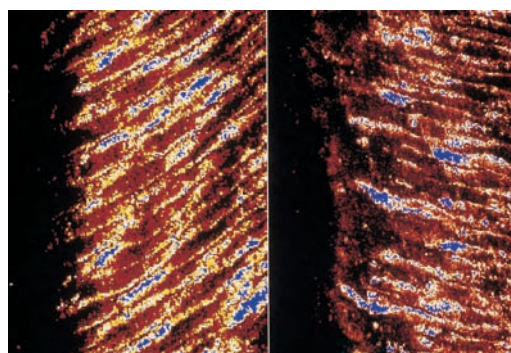


Fig. 6.20 Confocal laser scanning microscopic images of enamel adjacent to a bracket bonded with a glass ionomer cement. An eroded surface with almost intact prism structures can be seen. Areas with high reflection indicate periods of remineralization with fluoride following demineralization. (From Czochrowska *et al*, 1998)

incorporated into these materials in several ways, such as use of a mixture of water-soluble agents, use of dispersions of sparingly water-soluble agents, or as chemically bound agents. Whereas early attempts to incorporate fluoride into resin composites resulted in weaker bond strength, more recent research has shown no such effects. In fact, Steckel *et al* observed increased bond strength of brackets bonded with either fluoride-containing chemically cured or light-cured products. They speculated that perhaps the fluoride incorporated in the resin phase altered the surface tension of the liquid and thus resulted in increased wettability.

Most of the fluoride from resin composites is released during the first few days or weeks. Short-term experiments have shown significant reduction in caries development adjacent to brackets bonded with fluoride-releasing adhesives. However, the long-term effects of fluoride-releasing adhesives have been questioned owing to the small quantities of fluoride released. Also, fluoride-releasing sealants are marketed. Such sealants could be combined with conventional bonding agents, though the clinical importance of these agents has not been assessed.

Prevention of Caries Lesions Developed during Orthodontic Treatment

Debonding the orthodontic appliance reduces or eliminates the cariogenic environment on the labial surfaces, especially on the maxillary anterior teeth. However, it was shown that resin remnants were found on almost all teeth after debonding using different finishing techniques. This indicates a potential risk for plaque also to accumulate on the labial surface after debonding, perhaps in particular on the posterior and mandibular teeth where brackets are bonded close to the gingival margin. Lesions in these locations may thus progress after debonding if plaque is allowed to accumulate. Treatment of lesions that have developed during appliance therapy in the different sites of the dentition represents a clinical challenge, whether or not plaque may still accumulate on the surface.

It is well established that fluoride increases the initial rate of remineralization of early en-



Fig. 6.21 Discolored caries lesions developed during orthodontic treatment and recorded several years after debonding

amel lesions and then slows down the caries process. This is due to reaction of fluoride with minerals mainly in the surface of the lesion and results in arrest of the lesion. These arrested lesions will persist lifelong; they may exhibit a white color as in white spot lesions, or they may become yellowish or dark brown in color owing to uptake of exogenous stains (Fig. 6.21). This is supported by clinical data showing a higher prevalence of white spot lesions in areas with water fluoridation and in orthodontically treated patients several years after debonding. Whether complete remineralization may occur or not seems to be related to the type of lesion present. In one study the optical caries monitor was used. This is an instrument based on the stronger scattering of light in white spots compared to that in sound enamel. The study showed that initial lesions of the surface-softened type developed underneath orthodontic bands and that these lesions regained their scattering coefficient in an exponential manner after debanding. As no fluoride was used, it was concluded that regression of initial surface-softened lesions in the presence of saliva was a relatively rapid process.

Al-Khateeb *et al* followed seven patients with incipient enamel lesions developed during orthodontic treatment longitudinally for one year after debonding. These lesions were most likely of the subsurface type. No topical fluoride was recommended in addition to the daily use of a fluoride toothpaste. The changes in mineral content of the lesions were monitored using quantitative laser fluorescence.

During the one-year period of the study, the fluorescence radiance in the lesions increased and the area of the lesions decreased, indicating remineralization. However, complete regain of the lost minerals was not achieved. The conclusion from these two studies is that initial, surface-softened lesions developed rapidly, within weeks, and that these lesions can remineralize in saliva if they are kept plaque-free and not treated with concentrated fluoride agents. Also, lesions of the subsurface type developed during a longer period may remineralize to some extent in saliva. However, since lesions developed in association with orthodontic appliances during months of treatment may be several hundred micrometers deep, it is less realistic to expect complete remineralization. Furthermore, it is unlikely that the minerals are deposited in the same way as sound enamel. Consequently, light scattering from the partly remineralized lesion may not necessarily be identical to that for sound enamel. Perhaps the regression of these lesions as reported by some researchers is mainly due to surface wear rather than to deposition of minerals.

It has been suggested that acid etching of white spot lesions may increase the surface porosity and hence remineralization. Al-Khateeb *et al* produced white spot lesions in en-

amel *in vitro*, and investigated longitudinally the rate of remineralization in etched and non-etched lesions in the presence or absence of fluoride. The rate of remineralization was measured weekly for 12 weeks using a quantitative light-induced fluorescence method. The mineral profile of the remineralized tissue was analyzed with transverse microradiography, and the topography of the surface layer was studied with the scanning electron microscope. The study showed that the lesions persisted at the end of the experiment, and complete remineralization was not attained, irrespective of the treatment. The rate of remineralization varied significantly between the groups at the beginning of the experiment. Etched enamel exhibited more pronounced reduction of lesions than did non-etched enamel, especially in the absence of fluoride. Later the remineralization process slowed down, and at the end of the experiment no significant differences were found between the groups. The etched lesions retained a porous structure of their surface layer even after a long period of remineralization *in vitro*. Also, *in vitro* remineralization is known to proceed more rapidly than *in vivo* remineralization. Therefore, at this time there is insufficient evidence to recommend etching of lesions to enhance remineralization.

Conclusions and Clinical Recommendations

Without doubt, enamel decalcification is a major clinical problem in treatment with fixed appliances. It is most important to prevent caries lesions from developing during treatment. Once the lesions are established, in particular larger subsurface lesions, it is extremely difficult or even impossible to achieve complete remineralization. Fluoride will arrest these lesions, but in due time they may discolor. This is an unfavorable development and counteracts the beneficial effect of the orthodontic treatment altogether.

Fluoride is the most potent cariostatic agent available that can prevent the development of lesions. All orthodontic patients must brush daily with a fluoride toothpaste. Daily use of a fluoride mouthrinse is also recommended.

Optimal oral hygiene around the appliances is essential if the full effect of fluoride is to be obtained, since the cariogenic challenge is much higher and plaque pH is lower than in individuals without fixed appliances. Bands should be cemented with glass-ionomer cements because of the fluoride effect and higher bond strength. The use of glass-ionomer cements or resin-reinforced glass-ionomers for bracket bonding provides lower bond strengths than resin composites, but may be an alternative where the potential risk for decalcification exists. The long-term cariostatic effect of fluoride-releasing adhesives has not been sufficiently established, since most of the fluoride is released within the first few days or weeks. Therefore, topical fluoride in the form of solu-

tions, varnishes, or gels should be applied around the brackets on a regular basis. New formulas based on the most recent concepts of the mechanism of fluoride protection, or combinations with antimicrobials, may give

better clinical effects than conventional fluoride preparations. Agents depositing an acid-resistant coating on the enamel surface adjacent to the appliance may prevent lesion development almost totally.

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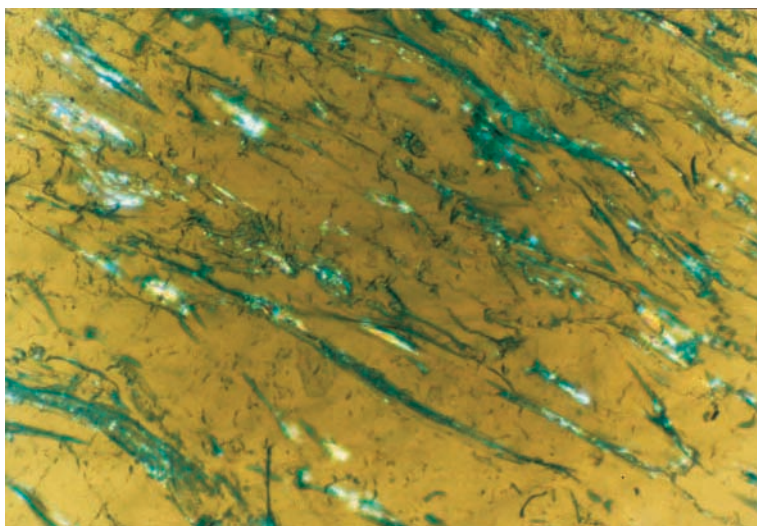
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7 Orthodontic Brackets

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George Eliades

William A. Brantley



Biofilm formed intraorally after an hour on polycarbonate bracket raw material (polarized light image) Original magnification $\times 50$

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Introduction

Orthodontic brackets bonded to enamel provide the means to transfer the force applied by the activated archwire to the tooth. The evolution of this appliance, originally manufactured from stainless steel, has demonstrated a unique progress curve characterized by extended quiescent periods interspersed with notably active periods.

The original treatment approach utilized a slot attached to a stainless steel band that was cemented to the tooth, and early attempts to modify this attachment resulted in wide base surfaces onto which a slot was soldered. This appliance was then bonded to the tooth with the use of epoxy resin. Although some reports list these advances as occurring in the 1960s, it was not until the late 1970s that direct bonding to enamel (Chapter 5) was widely accepted as a standard procedure to replace banding. The reasons for this significant delay arose from the initial reluctance of the orthodontic community to adopt the concept of etching tooth enamel. While the advances in bracket design and manufacturing include the three general aspects of base morphology, base-slot connection, and slot size characteristics, this chapter is concerned with the materials science of brackets, *i.e.*, mainly the first two general aspects. Slot prescriptions are named for their inventors who advocated a variety of angular values, depending upon treatment philosophy and mechanotherapeutic approaches.

The next stage of bracket evolution included modification of the base design to provide higher bond strength with adhesives, while concurrent efforts focused on decreasing the base surface, which at that time covered almost the entire labial mesiodistal tooth surface. While bracket manufacturing had traditionally employed mechanical deformation or wrought processing techniques to fabricate these appliances, further research led to the additional use of injection molding to fabricate cast brackets. A variety of standardized bracket types, such as twin, mini, and single appliances, were offered to the profession.

Subsequent research resulted in the introduction of brackets that had greatly improved aesthetic appearances compared to the metal brackets. These brackets have become popular

with the greatly increased number of adult orthodontic patients. The percentage of adult patients increased dramatically in the mid 1980s to 25 % of the total number of orthodontic patients, compared to very low percentages during the 1970s. Early commercially available aesthetic products included both plastic brackets and ceramic brackets fabricated from either polycrystalline or single-crystal alumina. While extensive commercial marketing of these products initially occurred during the mid 1980s, the first transparent bracket materials date back to the 1960s and the novel approaches and pioneering work of Newman and his co-workers.

The thicker profile of the initial ceramic brackets caused slight discomfort for some patients. However, the most serious clinical problem was the incidence of enamel damage during debonding and the occasional occurrence of bracket tie-wing fracture during therapy and subsequent debonding. Enamel cracking was promoted by the use of silane coatings on the base to increase bond strength, as well as by the use of crystal projections on the base to increase the active bonding surface available. Bracket wing fracture arose from the completely brittle nature of alumina, with crack propagation occurring more readily in the single-crystal (sapphire) form of this ceramic, as discussed in Chapter 1.

Plastic orthodontic brackets have also presented problems with the transfer of forces from an activated archwire. The low elastic modulus of the plastic can result in distortion of the appliance when the bracket is subjected to substantial forces *in vivo*. Some absorption of colorants was also noted with the first generation of these appliances. During the 1990s the manufacturers developed brackets with essentially no adverse clinical effects by modifying the design of the appliance and by using new reinforced polycarbonate plastic brackets. Recently, a wide array of polycarbonate brackets, with or without a metal slot, has become available. In contrast, there appears to have been a significant decrease in the number of brands of ceramic brackets. Tables 7.1 and 7.2 list some currently available plastic and ceramic bracket products.

Table 7.1 Some different types of commercially available plastic brackets^a

Product Name	Raw Material	Manufacturer/Country
Aesthetic Line	Polycarbonate-glass fibers	Forestadent/Germany
DB Fibre	Polycarbonate-composite	Leone/Italy
Elan	Polycarbonate-composite	GAC International/USA
Envision	Polyurethane-composite	Ortho Organizers/USA
Image	Polycarbonate-glass fibers	Gestenco/Sweden
Plastic	Polycarbonate	Dentaurum/Germany
Quantum	Plastic	Masel/USA
Value Line	Thermoplastic-polyurethane	OREC/USA
Spirit	Fiber-reinforced polycarbonate	Ormco/USA

^a Some products may not be available in all countries, and certain products may not be available at the time of publication. Additional information about the addresses for the above headquarters of the manufacturers is provided in the Appendix.

In describing bracket evolution, it is important to include the introduction of the self-ligating bracket. This was the result of an effort to develop a reliable appliance that would maintain steady force levels during activation while providing decreased frictional resistance and optimum three-dimensional control of tooth movement. An important characteristic of these appliances documented through

both *in vitro* and *in vivo* studies is the potential elimination of cross-contamination through the avoidance of elastomeric ligatures. Their use, however, has not become widespread, presumably because of the lack of interchangeable auxiliaries with conventional brackets and the necessity for maintaining an inventory of suitable utilities. From a materials science perspective, those materials are basi-

Table 7.2 Some different types of commercially available ceramic brackets^a

Product Name	Raw Material	Manufacturer/Country
Allure NSB	Polycrystalline alumina	GAC International/USA
Add another bracket: Contour	Polycrystalline alumina	Class One Orthodontics/USA
Clarity	Polycrystalline alumina	3M Unitek/USA
Eclipse	Alumina-plastic base	Masel/USA
Fascination	Polycrystalline alumina	Dentaurum/Germany
Hi-Brace	Polycrystalline zirconia	Toray Ceram/Japan
Intrigue	Polycrystalline alumina	Lancer Orthodontics/USA
Lumina	Polycrystalline alumina	Ormco/USA
MXi	Polycrystalline alumina	TP Orthodontics/USA
Signature	Polycrystalline alumina	RMO/USA
Starfire TMB	Single-crystal alumina	"A" Company-Ormco/USA
20/20	Polycrystalline alumina	American Orthodontics/USA

^a Some products may not be available in all countries, and certain products may not be available at the time of publication. Additional information about the addresses for the above headquarters of the manufacturers is provided in the Appendix.

cally identical to their conventional counterparts, and thus these products will not be described in this chapter.

Similarly, this chapter will not consider “recycled” brackets, although a more appropriate adjective would be “reused” or “reconditioned”. General usage of the term “recycled” implies the manufacturing of new brackets from raw material obtained from the original appliances. Information has been presented in the scientific literature comparing the material properties and slot dimensional alterations between as-received and re-used brackets. However, clinical utilization of these reconditioned appliances may be problematic in certain countries

owing to legal complications arising from the repeated use of a biomaterial. For example, manufacturers of biomaterials cannot currently obtain a CE notification for their products in the reused form, a mandatory condition for the marketing of products in the European Union. Also, significant variation with respect to processing/conditioning methods of used brackets among the “recycling” companies has been noted, while no suggestions or recommendations have been issued from any governmental organization. Thus, further clarification and documentation is necessary before this issue would be suitable for discussion in this textbook.

Metallic Brackets

Introduction and Early Research

Stainless steel brackets have been used for decades with highly successful clinical results. The morphology of the base, which is composed of a metal mesh, yields adequate adhesive bond strength values to enamel (discussed in Chapter 5) that meet the demands of *in vivo* orthodontic forces. Early studies, including research by Gwinnett and his colleagues, determined the optimum mesh size for increased bond strength. Extensive analyses of the rheological properties of the adhesive pastes have been performed, and it has been found that viscosity is principally controlled by the filler content volume. Manufacturers have incorporated a variety of mesh designs in their currently marketed products. Recent investigations, however, were not able to identify any differences in bond strength between conventional bracket bases and bases with more condensed mesh configurations. This may be because the base sizes chosen exceeded the optimum range for clinical use.

Advances in Metallic Brackets

Despite the clinically sufficient bond strength provided by conventional metal brackets, some attempts have focused on increasing the strength of the bracket-adhesive interface. The goal is to achieve bond longevity and integ-

rity throughout treatment for those special occasions where the currently available bond strength levels are insufficient. Droese and Diedrich have plasma-coated metal bracket bases having a variety of mesh designs as well as ceramic bracket bases. They reported that the enormously increased active surface area of the base resulted in much greater mechanical interlocking. For metal brackets, the non-mesh, plasma-sprayed bases had tensile adhesive bond strengths similar to those for unsprayed mesh bases. However, plasma-sprayed ceramic brackets did not yield similar results, and it was concluded that these brackets are not good candidates for this procedure.

There have been some potentially alarming reports on the corrosion potential of the AISI type 316L austenitic stainless steel alloy currently used for bracket manufacturing. This alloy contains 16–18% Cr, 10–14% Ni, 2–3% Mo and a maximum of 0.03% C (values in wt%); the “L” designation refers to the lower carbon content compared to type 316 stainless steel, which contains a nominal maximum amount of 0.08 wt% C. The 316L stainless steel contains somewhat more nickel, somewhat less chromium, and substantially less carbon than the AISI types 302 and 304 stainless steel archwire alloys (Chapter 4), along with a small amount of molybdenum that is not present in the latter. (All of these stainless steel alloys also contain a nominal amount of 2 wt% Mn.) Although the 316L stainless steel bracket alloy



Fig. 7.1 Corrosion attack of 316L stainless steel alloy identified following debonding where corrosion products have diffused into the adhesive layer, causing discoloration

has performed well clinically, some corrosion of this material may be identified in the form of discoloration of the underlying adhesive layer (Fig. 7.1). Majier and Smith have attributed this effect to the diffusion of corrosion products from the bracket base to the adhesive, noting also the potential for enamel discoloration. As discussed in Chapter 4, the corrosion resistance of stainless steel is provided by a passive surface film of chromium oxide; the corrosion resistance of titanium and its alloys is provided by an analogous passive film of titanium oxide. While the addition of molybdenum to the 316L stainless steel alloy provides further protection from crevice and pitting corrosion, the chromium oxide passive films are not as stable as their titanium oxide counterparts.

Clinical interest in the *in vivo* corrosion attack of metal brackets derives from the potential adverse biological consequences, as discussed in Chapter 15. The chief concern is the release of nickel ions during corrosion of stainless steel. It was previously noted in Chapter 4 that nickel is incorporated in the compositions of all austenitic stainless steel alloys to stabilize the austenite phase.

Aesthetic Brackets

Many types of aesthetic brackets have been introduced during the past decade. Appliances fabricated from alumina and zirconia ceramics, as well as a variety of plastic brackets, have been marketed. Consideration of the compositions, manufacturing, and properties of these brackets may clarify several issues pertinent to their clinical performance.

A 2205 stainless steel alloy that contains half the amount of nickel found in the 316L alloy has recently been proposed by Oshida, Moore and their colleagues as an alternative for orthodontic brackets. The 2205 stainless steel alloy has a duplex microstructure consisting of austenitic and delta-ferritic phases, and is harder than the 316L alloy. Moreover, the 2205 alloy demonstrated substantially less crevice corrosion than the 316L alloy when coupled with NiTi, β -titanium, or stainless steel archwires in an *in vitro* immersion test using an aqueous NaCl solution at 37 °C.

Use of the 2205 stainless steel alloy for brackets also follows from recent research by Matasa, who measured the microhardness values (Chapter 1) of metallic brackets to obtain information about the relative strengths of the bracket alloys. It was found that the 316L alloy had much lower hardness compared to the PH (precipitation-hardening) 17-4 stainless steel bracket alloy, although the former had significantly higher corrosion resistance. Further research is needed to find the stainless steel alloy with an optimum combination of strength and corrosion resistance for orthodontic brackets.

Some recently reported evidence on the feasibility of manufacturing titanium brackets by metal injection molding (MIM) may open new horizons for the metallic appliances. The brackets tested exhibited mechanical properties and bond strengths equivalent to or better than that of stainless steel brackets, while the new alloy provides better corrosion resistance and absence of nickel leaching.

As the process of optimizing materials for orthodontic applications gains increasing interest, a new generation of metallic appliances may be developed minimizing the concerns about adverse biological reactions.

Plastic Brackets

The first plastic brackets were manufactured from unfilled polycarbonate and introduced during the early 1970s. Unfortunately, these brackets had a tendency to undergo creep deformation when transferring torque loads generated by archwires to the teeth. Ceramic-

reinforced, fiberglass-reinforced, and metal slot-reinforced polycarbonate brackets were subsequently introduced to alleviate this problem. Another problem was discoloration of the first-generation unfilled polycarbonate brackets during clinical aging.

The reinforced polycarbonate brackets were also introduced in response to reports of enamel damage by ceramic brackets. The primers that were used to prepare the base for bonding

have gradually been eliminated so that this clinical step would be avoided during bracket placement on the etched enamel surface. These primers contain low-molecular-weight dimethacrylates and methyl methacrylate, producing a surface that facilitates micromechanical interlocking (Fig. 7.2).

While the metal slot-reinforced polycarbonate brackets appear to be capable of generating the desired torque on teeth under clinical

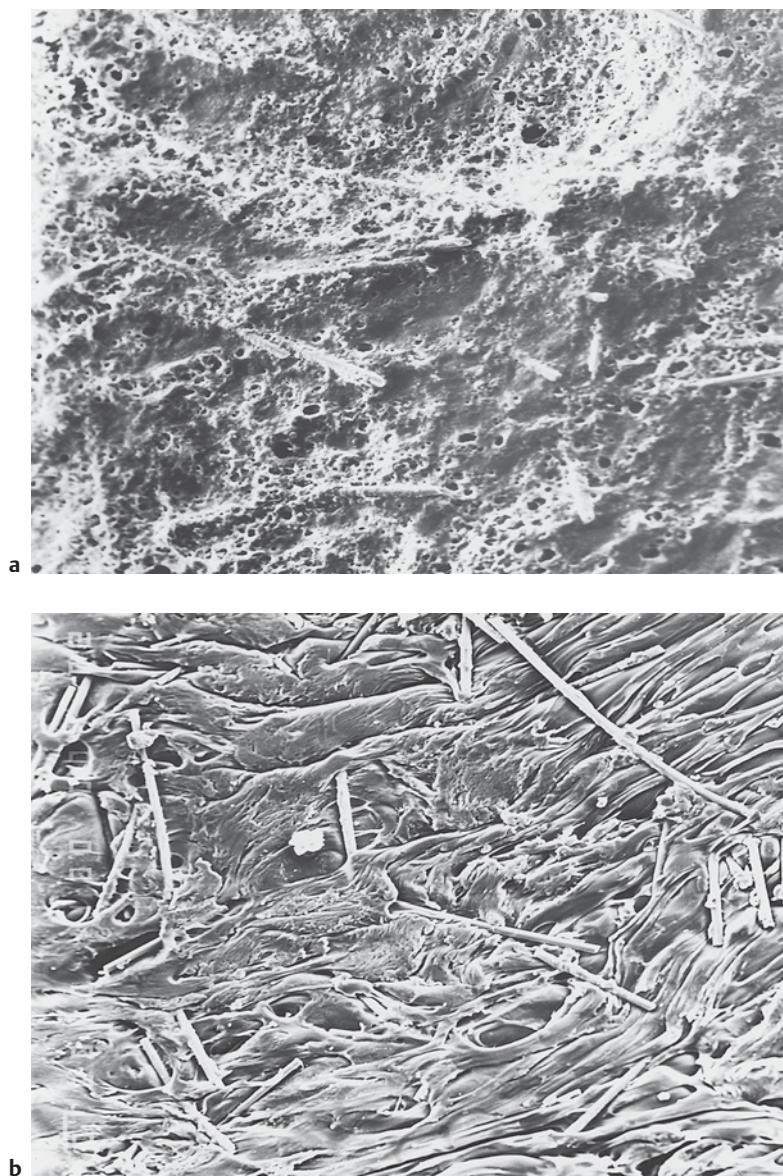


Fig. 7.2 Secondary electron images of the base of a polycarbonate bracket. **(a)** As-received. Original magnification $\times 60$. **(b)** Following application of a methacrylate-based primer, depicting the dramatically increased roughness used to facilitate micromechanical interlocking with the adhesive. Original magnification $\times 60$. The plasticity (flow) of the primer greatly increases the surface roughness and exposes some fibers from the polycarbonate matrix

conditions, problems have been reported with the integrity of the slot periphery. Some of the metal slots have a level of surface roughness that may significantly affect the archwire-bracket sliding friction (Fig. 7.3). A beneficial consequence of the relatively low elastic modulus of polycarbonate is that the load applied during debonding of the plastic brackets results in a peel-off effect, mimicking the debonding behavior of metal brackets (Figs. 7.4 and 7.5).

Further research is needed on the bond strength, torque delivery, clinical aging, and creep properties of the currently available polycarbonate brackets.

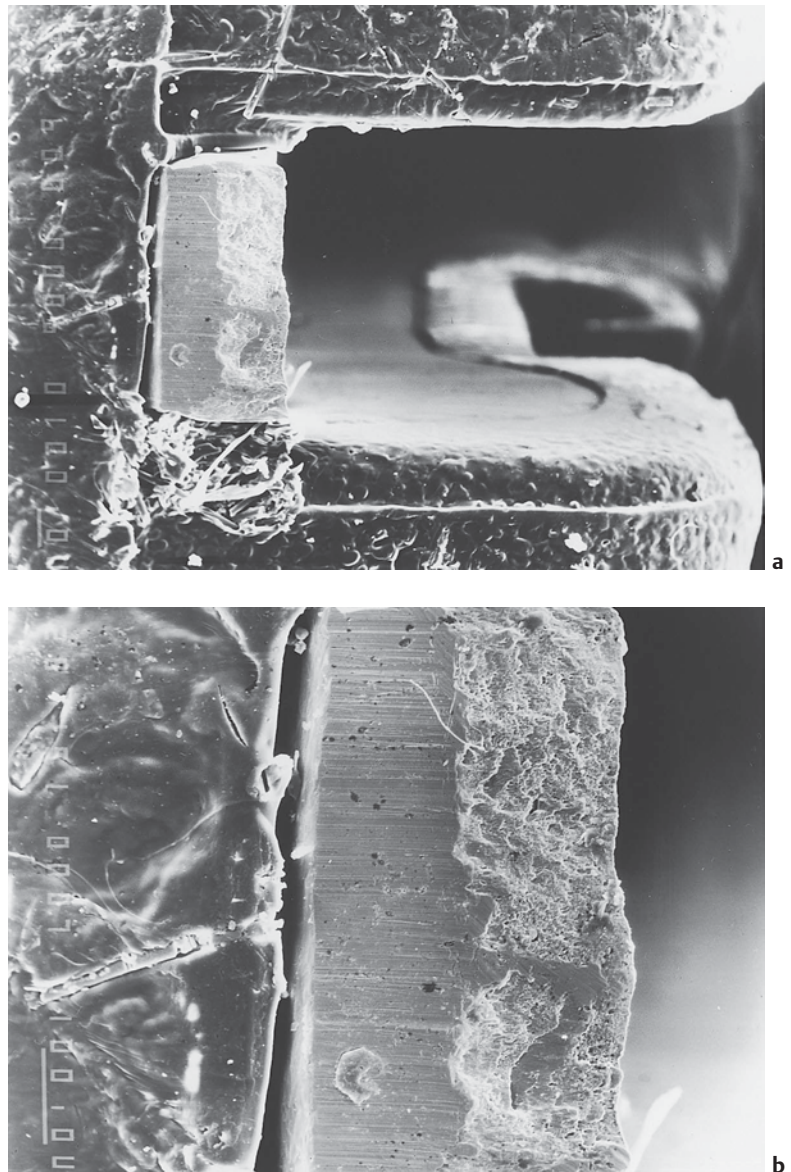


Fig. 7.3 Secondary electron images of a polycarbonate bracket with metallic slot, demonstrating increased roughness of the slot surface opposing the archwire. (a) Lateral view. Original magnification $\times 60$. (b) Lateral view. Original magnification $\times 150$. Note the incomplete adaptation of the metallic slot base to the bracket wall

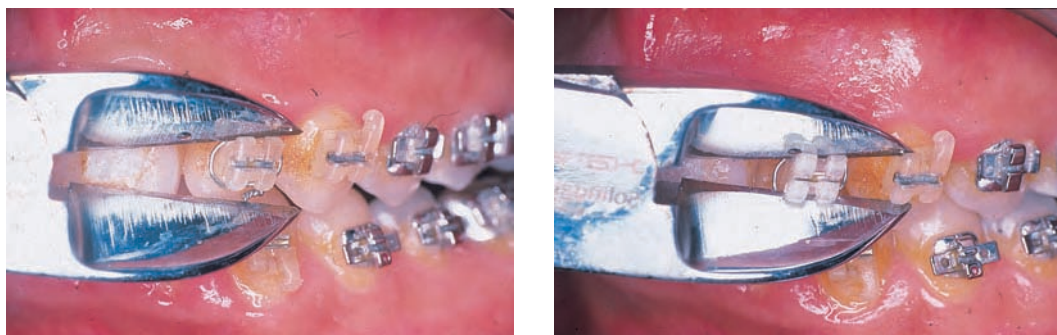
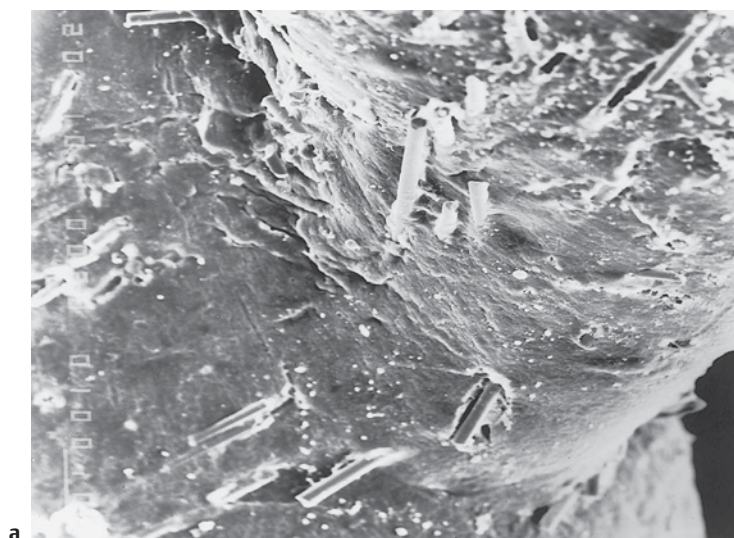


Fig. 7.4 Polycarbonate bracket exhibiting bending distortion during debonding, where the pattern mimics the peel-off debonding of stainless steel brackets. Note the bending of the bracket wings



a



b

Fig. 7.5 Secondary electron images of the debonded polycarbonate bracket shown in Fig. 7.4. Original magnification $\times 48$. (a) Twisting-like bending of the tie-wing caused by application of the debonding forces. Note the breakage and projection of the fibers caused by twisting of the tie-wing following debonding. (b) Distortion of the slot width as a result of the compressive force applied during debonding

Ceramic Brackets

Composition, Structure and Manufacturing Process

Most ceramic brackets are made of high-purity aluminum oxide (alumina), and the brackets are available in both polycrystalline and single-crystal (sapphire) forms. Alumina brackets were first introduced in the late 1980s. Ceramic brackets fabricated from polycrystalline zirconium oxide (zirconia) were subsequently manufactured in Australia and Japan.

Polycrystalline alumina brackets are manufactured by first combining a suitable binder with aluminum oxide particles (average of 0.3 μm size) so that this mixture can be molded into the shape of a bracket. This molded mixture is then heated (fired) at temperatures in excess of 1800 °C to burn out the binder and achieve sintering of the particles. Diamond cutting tools are then used to machine the slot dimensions. Heat treatment is subsequently performed to relieve stresses caused by the cutting and to remove surface imperfections resulting from the manufacturing processes.

The sintering produces a polycrystalline alumina microstructure with grain boundaries (Chapter 1), resulting in some translucency. There is loss of light transmission through the ceramic because of a small variation in refractive index with crystallographic direction within grains and scattering processes at the grain boundaries. Optical properties and strength are inversely related for the polycrystalline alumina ceramics: the larger the individual grains in the microstructure, the greater is the ceramic translucency. However, when the grain size approaches 30 μm , the material becomes substantially weaker. Heat

treatment after machining the slots must be carefully controlled to prevent grain growth that would degrade the physical properties. While the manufacturing process readily allows alumina brackets to be molded to the desired geometry, structural imperfections at the grain boundaries or trace amounts of sintering aids (concentrations as low as 0.001 %) can serve as sites of crack initiation under stress.

The first step in the manufacture of the single-crystal brackets is the slow cooling of molten high-purity aluminum oxide under controlled conditions from temperatures above 2100 °C. The resulting bulk single-crystal alumina in rod or bar form is then milled into brackets using diamond cutting, Nd:YAG lasers, or ultrasonic cutting. The single-crystal brackets are also subsequently heat treated to remove surface imperfections and stresses created by the milling process.

The single-crystal alumina brackets contain less impurities than are found in the polycrystalline alumina brackets, which require the presence of sintering aids during manufacturing. Single-crystal brackets also have excellent optical clarity owing to the absence of internal grain boundaries, although there is a minor amount of birefringence resulting from variation of the refractive index with crystallographic direction. Physical properties of single-crystal and polycrystalline alumina brackets are listed in Table 7.3. Once fracture initiation has occurred at Griffith flaws (Chapter 1) under sufficiently high local stresses, single-crystal alumina has lower resistance to crack propagation than does polycrystalline alumina, where the advancing cracks follow irregular paths along grain boundaries. Figures 7.6 and 7.7 are scanning electron microscope (SEM) photographs of fractured tie-wings, illustrating the differ-

Table 7.3 Mechanical properties of aluminum oxide

Property	Single-Crystal Alumina (sapphire)	Polycrystalline Alumina (99.9 % purity and sintered)
Modulus of elasticity (GPa)	430	390
Bending strength (MPa)	630	280
Compressive strength (MPa)	2100-4100	2400
Tensile strength (MPa)	1800-2600	210-310

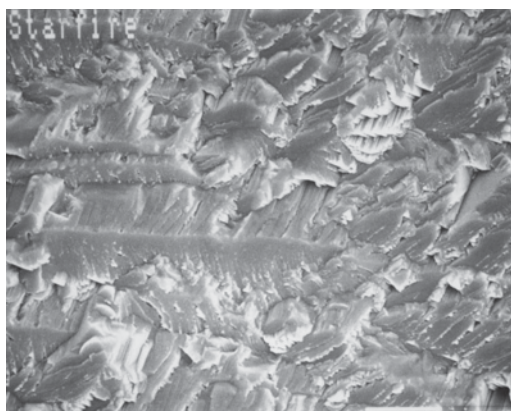


Fig. 7.6 Secondary electron image of the tie-wing fracture site for compressive loading of a Starfire TMB single-crystal alumina bracket. Scale bar length = 10 μm . (From Sonneveld *et al*, 1993. An abstract describing this study is found in Sonneveld *et al*, 1994)

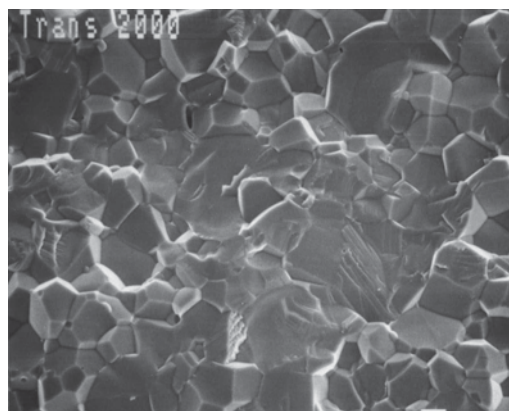


Fig. 7.7 Secondary electron image of the tie-wing fracture site for compressive loading of a Transcend 2000 polycrystalline alumina bracket. Scale bar length = 10 μm . (From Sonneveld, 1993. An abstract describing this study is found in Sonneveld *et al*, 1994)

ence in crack propagation behavior for single-crystal and polycrystalline alumina brackets.

The strength of both single-crystal and polycrystalline alumina can be increased by eliminating surface flaws that can serve as sites of stress concentration and fracture initiation. Decreasing the grain size will also increase the strength of polycrystalline alumina. The properties of surgical grade alumina are summarized in Table 7.4.

There has been interest in zirconia brackets because of the possibility of achieving much higher values of fracture toughness than are possible for polycrystalline alumina brackets, as discussed at length in a later section. The

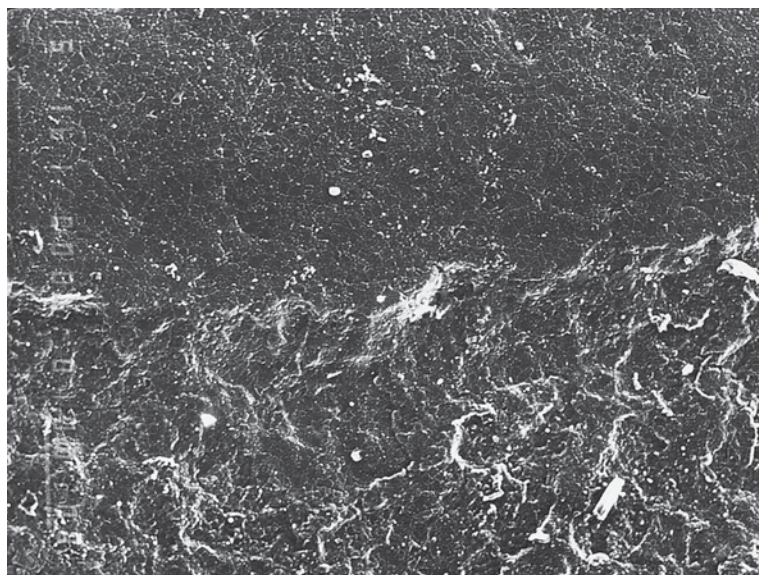
polycrystalline zirconia brackets are manufactured by impression molding, followed by hot isostatic pressing. Yttrium oxide-partially stabilized zirconia (YPSZ) can be obtained in bulk form by sintering (without pressure up to 95% of the theoretical density) a mixture of ultrafine zirconia powder (average starting particle size of 0.2 μm) and 5 wt% yttrium oxide. A polycrystalline microstructure with an average grain size of about 0.5 μm is obtained, and hot isostatic pressing is subsequently employed to remove residual porosity with limited additional grain growth. Table 7.3 compares the properties of surgical grade alumina and YPSZ in bulk form.

Table 7.4 Properties of surgical grade alumina and yttrium oxide-partially stabilized zirconia (YPSZ)

Property	Alumina (ISO/Dis 130/D13)	YPSZ Pressureless Sintering	YPSZ Sintered and Hot Isostatically Pressed
Density (gm/cm^3)	3.90	6	6.1
Average grain size (μm)	< 7	< 1	< 0.5
Microhardness (Vickers)	2000–3000	1000–1200	1000–1300
Elastic modulus (GPa)	380	200	200
Bending strength (MPa)	400	900	1200
Fracture toughness K_{Ic} ($\text{MPa} \cdot \text{m}^{1/2}$)	5–6	9–10	9–10

From Christel *et al*, 1989. Reprinted with permission from the Journal of Biomedical Materials Research

Fig. 7.8 Secondary electron image of the base of a polycrystalline alumina bracket employing large recesses for mechanical interlocking with the adhesive resin. Original magnification $\times 160$



Base Morphology

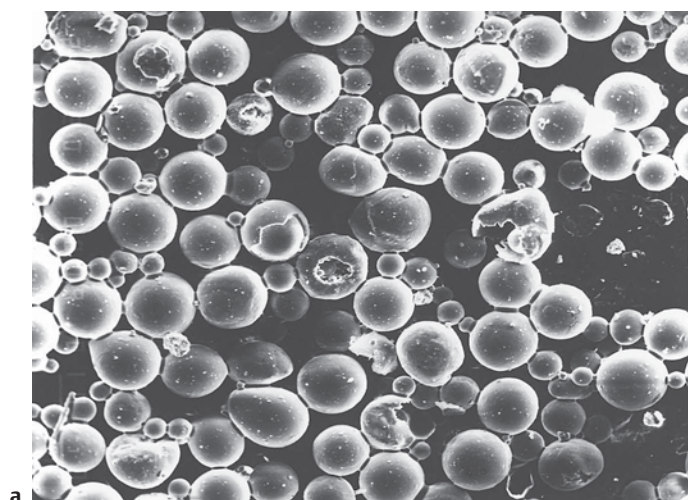
Several papers published during the mid-1990s dealt with the description of the ceramic bracket base design, structure, and composition, and the associated mechanisms for retention to the etched enamel. Microscopic and spectroscopic analyses employed for study of the structure and morphology of the bases have provided some clarification of the bracket manufacturing processes. The bonding mechanisms that have

been identified may be classified into three major categories:

- Mechanical retention employing large recesses (Fig. 7.8)
- Chemical adhesion facilitated by the use of a silane layer (Fig. 7.9)
- Micromechanical retention through the utilization of a number of configurations, including protruding crystals, grooves, a porous surface, and spherical glass particles (Fig. 7.10).

Fig. 7.9 Incident polarized light image of the base of a single-crystal ceramic bracket covered with an island of a silane layer, illustrating a birefringence effect. Bright field image, crossed polarizers. Original magnification $\times 50$

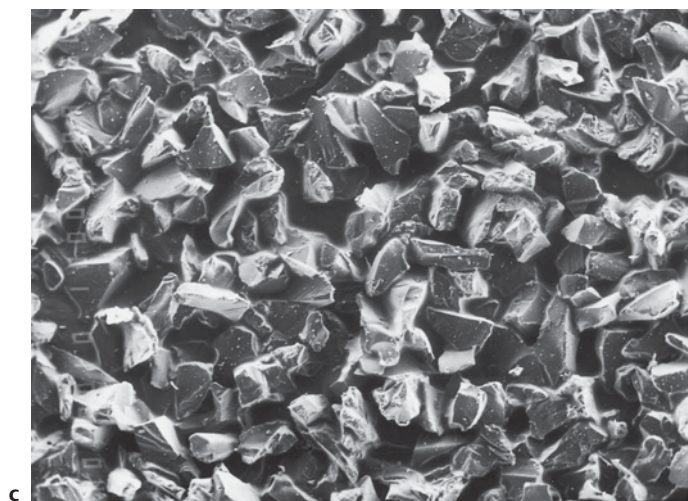




a



b



c

Fig. 7.10 Bases of polycrystalline brackets employing various protrusion designs for micromechanical interlocking with the adhesive. (a) Base with spherical particles. Secondary electron image. Original magnification $\times 200$. (b) Cross section of the base of the brackets shown in (a), illustrating the spherical particle protrusion. Secondary electron image. Original magnification $\times 200$. (c) Sharp-edged crystal protrusions. Secondary electron image. Original magnification $\times 60$.

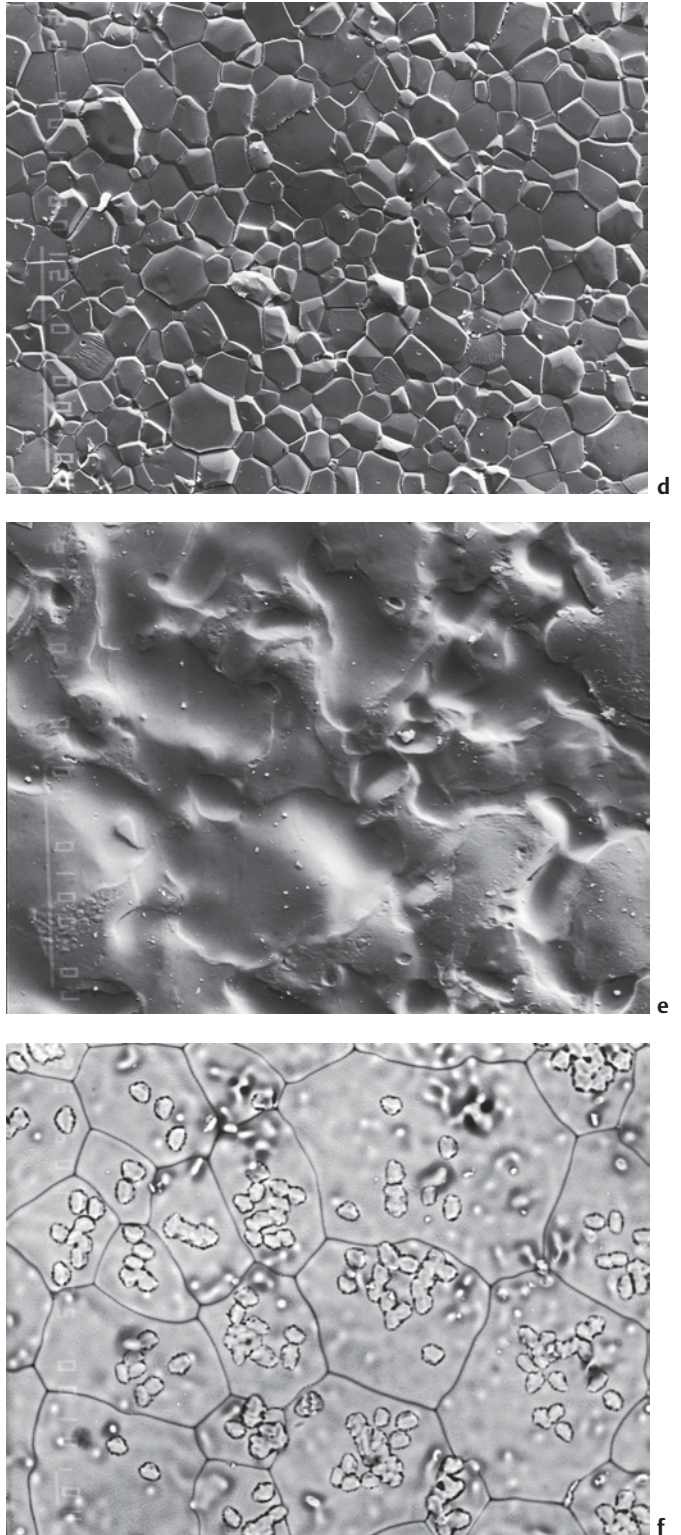


Fig. 7.10 (d) Detail of a flat surface of a bracket base with large recesses. Note the excellent resolution of the crystal boundaries. Secondary electron image. Original magnification $\times 400$. (e) Plastic base of a polycrystalline ceramic bracket with a flexible base. Note rounded irregularities. Secondary electron image. Original magnification $\times 400$. (f) Compositional backscattered electron image of a smooth polycrystalline alumina bracket base, demonstrating particle aggregates possibly due to incomplete sintering. Original magnification $\times 600$

A combination of two or more of the above mechanisms may also be employed to achieve further strengthening of the interfacial region between the base and adhesive and yield increased bond strength.

Smooth bracket base surfaces should better distribute the shear stresses over the entire adhesive, while minimizing localized areas of stress concentration. In the presence of strong chemical adhesion, such localized stresses would promote cohesive resin failures, resin/enamel failures, and even cohesive bracket fractures. The irregular-shaped microparticles on the bases do not appear to offer sites for local stress concentrations to initiate failure, particularly when these particles are covered by the adhesive layer. Nonetheless, Katona and co-workers (Chapter 2) have shown evidence of the inhomogeneous stress distribution within the underlying adhesive layer.

The clinical importance of the design and structure of the bracket base is twofold. First, the longevity and integrity of the adhesive bond depend strongly on the base. Second, and more important, studies have demonstrated the pivotal role of the base for enamel damage observed following debonding.

Initially, manufacturers sought the highest bond strengths attainable for alumina brackets, since early failure of the brackets *in vivo* would be a frustrating event for the clinician and the patient, adversely affecting the reputation of the appliance. Thus, manufacturers incorporated combinations of retention mechanisms, with the goal of achieving long-term bracket bonding. However, when the first alumina brackets were debonded for patients, enamel cracks and cohesive bracket failures were frequently observed. These clinical case reports were supported by the results of *in vitro* studies of the debonding behavior and mechanical properties of the brackets.

Consequently, manufacturers modified the design of the ceramic bracket bases, using the following three major strategies:

- An increase in the size and a decrease in the number of protruding crystals or projected complexes, thus reducing the mechanical retention of the interfacial layer
- Elimination of the silane coating to reduce the adherence between the adhesive and bracket

- Combination of the relatively rigid ceramic bracket with a more flexible base consisting of a low elastic modulus polycarbonate or other polymeric material

These remedies have greatly reduced the incidence of enamel damage or bracket fracture during debonding at the conclusion of orthodontic treatment. At the time of writing, a period of almost four years has elapsed since the last report of significant enamel damage during debonding in the orthodontic literature. However, numerous bond strength studies continue to be published as manufacturers introduce new bracket and adhesive products. Because of the original negative publicity, manufacturers often focus on debonding features as the most important aspect of their ceramic brackets. As noted previously, such concerns stimulated the development of fiber-reinforced polycarbonate brackets that provide safe debonding. Techniques for debonding ceramic brackets are discussed in a later section of this chapter.

A study has focused on the effects of newly introduced sonic brushes and cleaning tools on the bond integrity for orthodontic aesthetic brackets. There was some concern for orthodontic patients using these mechanical cleaning devices because of the possibility of adhesive bond degradation. Results have shown that there is no detrimental effect on bond strength.

Silane Coating of Bracket Bases

The coupling agent γ -methacryloxypropyltrimethoxysilane (γ -MPTS) has been widely used in dentistry as a coupling agent for promoting chemical adhesion between surfaces. The γ -MPTS is hydrolyzed to the corresponding silanol. A limited number of silanol groups per silane molecule are hydrogen-bonded to the water layer adsorbed on the base surface. Few -Si-O-Al- bonds may then be formed as well, especially after prolonged, high-temperature silanization treatment during the manufacturing process. Side-chain silanols are condensed, establishing a siloxane network that stabilizes the structure. Owing to the silanol orientation toward the bracket base, methacrylate groups are placed in a configuration that favors cross-linking with the methacrylate-

based adhesive. This silane is the coupling agent between the inorganic filler particles and polymer matrix of resin composites; it permits the repair of fractured porcelain surfaces in porcelain-fused-to-metal restorations, and provides bonding of ceramic and glass-ceramic crowns, inlays, and onlays. Under ambient conditions, the bonding arises from two mechanisms: silanol groups of the hydrolyzed silane adhere to the hydration layer of the inorganic surfaces, while methacrylate groups of the silane copolymerize with the methacrylate resin matrix, possibly forming covalent bonds.

Silane coating of the ceramic bracket bases has been identified for a limited number of commercially available products that have been studied in the past. Examination of the bracket bases revealed discontinuous zones of a silane layer having nonuniform thickness (Fig. 7.9). The base morphology of brackets employing a silane coating was found to vary from smooth to relatively rough with large recesses to extremely rough with projected crystals and multiple grooves. The last combination yielded the highest bond strength but resulted in enamel damage during debonding, and has been abandoned in currently marketed orthodontic brackets.

Optical Properties

The use of transparent brackets has stimulated efforts to combine this attractive option of treating aesthetics-conscious individuals with the advantages of light-cured adhesives (Fig. 7.11). Apart from aesthetics, however, the amount of the photocuring light transmitted through a bracket may affect the properties of the light-cured adhesive. The optical transmittance of these brackets and its effect on the curing efficiency of the underlying light-cured adhesive has been examined. For example, the direct light transmittance at the peak optical absorption wavelength (468 nm) of the photoinitiator camphoroquinone was found to range between 35% and less than 5% for a single-crystal alumina bracket and several polycrystalline alumina brackets, respectively. This difference arises from the presence of grain boundaries in the latter brackets, which cause light scattering and reduction in the intensity of the light beam reaching the adhesive paste. The variation in direct light transmit-



Fig. 7.11 Polycrystalline alumina (first, third, and fourth from left), single-crystal alumina (second from left), and zirconia (right) aesthetic brackets demonstrating various degrees of optical translucency

tance among the different polycrystalline alumina brackets is due to differences in bracket geometry and microstructural grain size. Color-coded holders intended for identification and handling of these brackets also caused severe light blockage, and their use should be avoided when these brackets are bonded with light-cured adhesives.

When the same brackets were examined in the diffuse light transmittance mode, the percentage transmittance values at 468 nm were almost quadrupled for the polycrystalline alumina brackets and doubled for the single-crystal alumina bracket. The use of an integrating sphere for the diffuse light transmittance experiments results in the detection of virtually all of the light scattered through the bracket, and therefore this method more accurately represents the amount of light transmitted through the bracket during photopolymerization. It is interesting to note that the brackets exhibiting the least translucency had similar low values for both the direct and diffuse light transmittance measurements. Despite the wide variation of the light transmittance values among the alumina brackets studied, a much narrower range was found for the degree of cure of the resin adhesive. It was proposed that under the usual conditions present in the orthodontic bonding environment, a critical value for light transmittance, ranging between 30% and 40%, must be attained to induce adequate polymerization of the adhesive. Additional information on the degree of cure and associated properties of orthodontic adhesives is presented in Chapter 10.

Fracture Toughness and Impact Resistance

As discussed in Chapter 1, fracture toughness is a measure of the strain energy-absorbing ability prior to fracture for a brittle material. It is related to the level of tensile stress that must be exceeded at the tip of a crack before propagation results in material failure. It was explained in Chapter 2 that the fracture toughness (which is the critical stress-intensity factor at the tip for crack propagation) is given by the product of the fracture stress (σ_F) and $\sqrt{\pi a}$, where a is the length of the crack whose propagation results in failure. The higher the fracture toughness, the more difficult it is to propagate a crack in the material.

As explained in Chapter 1, the alumina ceramics used in the manufacture of orthodontic brackets contain strong, directional covalent bonds that do not allow permanent deformation or ductility by the movement of dislocations as found in metals. When these ceramics are subjected to their maximum elastic stress levels, brittle failure occurs in which interatomic bonds at the tips of flaws rupture, and the material fails by crack propagation.

Alumina brackets are very susceptible to crack initiation at minute imperfections or regions where material impurities have accumulated. As noted previously, crack propagation is relatively unimpeded in single-crystal alumina brackets compared with polycrystalline alumina brackets. Fracture surface energies are higher for polycrystalline alumina than for single-crystal alumina because of the irregular paths of crack propagation along the grain boundaries in the former (Figs. 7.6 and 7.7). Using the Vickers indentation technique (Chapter 2), mean values of 3.60 and 5.22 MPa·m^{1/2} have been obtained for two brands of polycrystalline alumina brackets.

The yttrium oxide-partially stabilized zirconia (YPSZ) industrial ceramics have remarkable ability to absorb impact energy and resist fracture because of the effect of phase transformation toughening. Zirconium oxide can exist in three different crystal structures: cubic, tetragonal, and monoclinic, each of which has a temperature range for stability. During heating, the monoclinic form, which is the stable phase at room temperature, is first transformed into the tetragonal phase in the 1000–1100 °C tem-

perature range, and then into the cubic phase at temperatures above 2000 °C. The 3% volume increase for the tetragonal-monoclinic transformation during subsequent cooling after sintering is sufficient to cause fracture of a zirconia specimen. The addition of stabilizing oxides, as calcium oxide, magnesium oxide, and yttrium oxide can inhibit this phase transformation, so that the tetragonal structure can be maintained in a metastable state at room temperature. The transformation of grains having the tetragonal structure to the monoclinic structure, which would cause a volume increase, is prevented because of compressive stresses applied by adjacent grains. Using Y₂O₃ as a stabilizing agent, industrial YPSZ composed of 100% small metastable grains has been produced. The stress fields at the tips of propagating cracks in the YPSZ ceramics cause a stress-induced transformation from the metastable tetragonal structure to the equilibrium monoclinic structure that efficiently absorbs the strain energy in the material. Moreover, the resulting volume expansion results in compressive stresses at the edge of the crack front, thereby requiring extra energy for the crack to propagate further. Accordingly, very high values of fracture toughness in the range of 9–10 MPa·m^{1/2} have been reported for YPSZ ceramics (Table 7.4).

However, Tilson and his colleagues, using the Vickers indentation technique, have shown that zirconia brackets (Hi-Brace, Toray Ceram, Yamaura, Japan) have much lower mean fracture toughness of approximately 3.92 MPa·m^{1/2}. A typical Vickers indentation used to measure the fracture toughness of a zirconia bracket is shown in Figure 7.12. This value lies within the range of reported fracture toughness values for polycrystalline alumina brackets. X-ray diffraction analyses of the zirconia brackets have revealed substantial quantities of the high-temperature cubic form of zirconia, in addition to the tetragonal phase, as shown in Figure 7.13. Consequently, the zirconia brackets are not fully YPSZ ceramics, which suggests that further research is needed to determine the optimum conditions for manufacturing these appliances. Regions of incompletely sintered starting powder particles were also observed near some Vickers indentations in the zirconia brackets. A scanning electron microscope (SEM) photograph of a large void in a zirconia bracket is

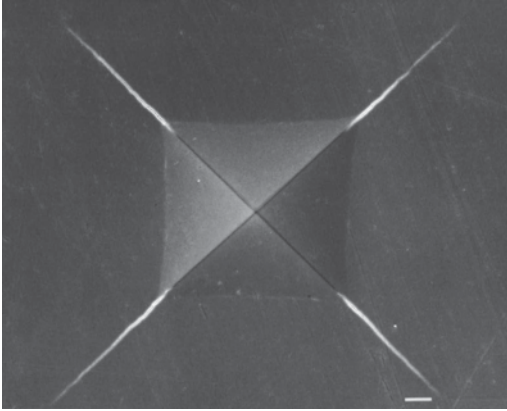


Fig. 7.12 A representative Vickers indentation in a polished zirconia bracket surface. Scale bar length = 10 μm . (From Tilson, 1994. An abstract describing this study is found in Tilson *et al*, 1995a)

shown in Figure 7.14. Acceptance of the zirconia brackets has not been widespread because of their inferior aesthetics (greater opacity and yellowish tint) compared to the polycrystalline alumina brackets.

Matasa has published a study investigating the impact resistance of several alumina brackets in which the testing mode simulated the accidental blows often occurring under clinical conditions. Impact loading of ceramic brackets has not been employed in previous studies where the strength was determined under the relatively slow rates of loading provided by standard mechanical testing machines (Chapter 2). Alumina brackets having a smooth face, polycrystalline microstructure, and relatively bulky design had increased impact resistance. Single-crystal alumina brackets and brackets with twin attachments, extended pro-

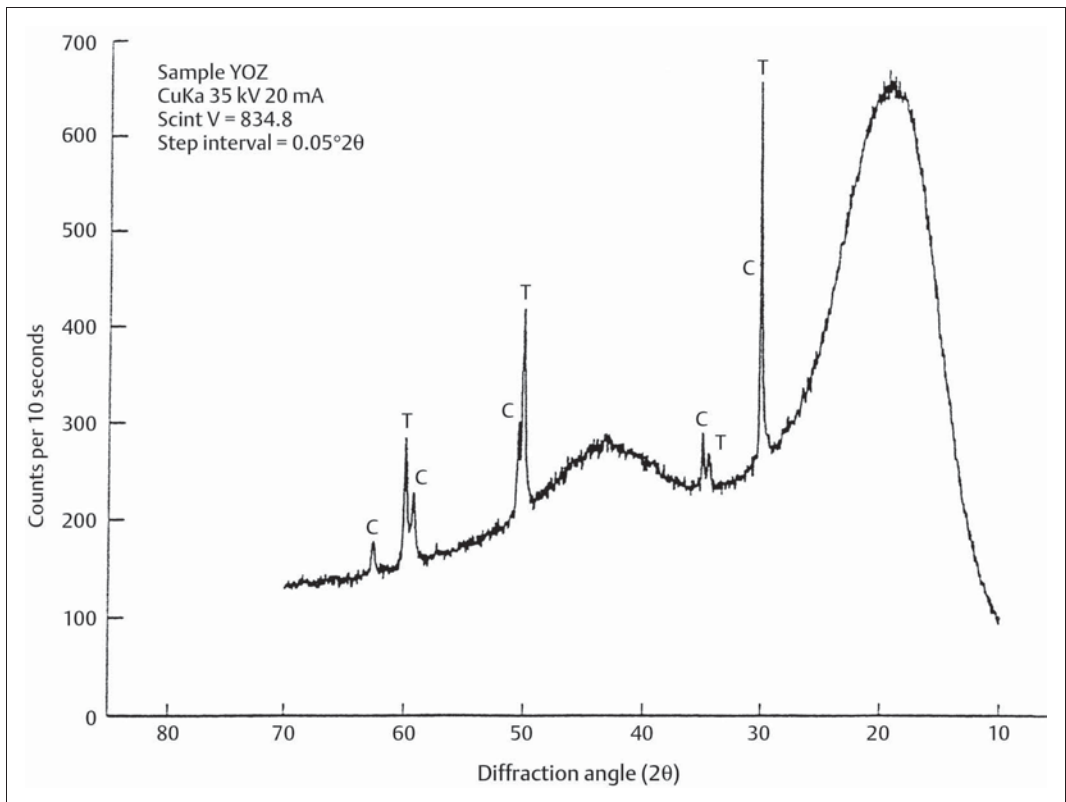


Fig. 7.13 X-ray diffraction pattern for a zirconia bracket. Peaks corresponding to the tetragonal (T) and cubic (C) zirconia phases have been labeled. The varying background with two broad peaks arises from the amorphous resin used for embedding the bracket when preparing the specimen for XRD analysis. (From Tilson, 1994. An abstract describing this study is found in Tilson *et al*, 1995b)

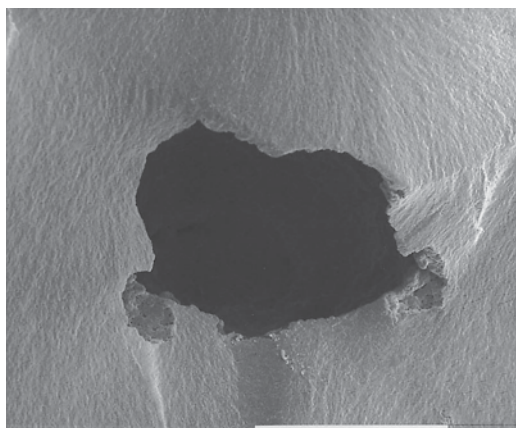


Fig. 7.14 Secondary electron image of a large void in a zirconia bracket. Scale bar length = 100 μm . (From Tilson, 1994. An abstract describing this study is found in Tilson *et al*, 1995b)

files, and protruding tie-wings presented the least impact resistance. More quantitative studies of the impact resistance of ceramic brackets, using novel testing methodologies, would be worthwhile.

Tie-Wing Strength

Tie-wing fracture of ceramic brackets is a major concern for the orthodontist, since the appliance becomes ineffective and ligation of the archwire to the bracket is no longer achievable. Debonding of the fractured bracket is required, followed by rebonding of a new bracket. Additional chairside time must be spent by the orthodontist to perform these procedures, in addition to the risk of enamel damage involved in removal of the adhesive resin.

Photoelastic studies and finite-element analyses (FEA) have shown that the bases of the tie-wings are generally the locations of concentrated stresses when forces are applied to the bracket by the orthodontist. Tie-wing fractures have been much more common for the single-crystal alumina brackets because of their lower resistance to crack propagation. Clinical procedures that may scratch or otherwise damage the surfaces of alumina brackets further reduce fracture toughness and predispose the bracket to eventual failure.

A limited number of studies have been performed to determine the force levels that cause tie-wing fracture under clinically relevant conditions and to examine the fractured brackets microscopically. Sufficiently high compressive loads applied to bracket tie-wings reveal the brittle nature of single-crystal and polycrystalline alumina. While such tests can provide useful information, the fracture loads have been found to depend upon the pattern of tie-wing fractures for the single-crystal and polycrystalline alumina appliances. Caution must be exercised in designing the loading fixture for these types of tests, since tie-wing fractures typically occur at relatively low levels of force where stress concentrations are involved.

Sonneveld and his colleagues compared the breaking force in compression for alumina and zirconia brackets. A steel rod machined with a cone-shaped recess having an internal apex angle of approximately 120° was used to achieve nearly equal engagement of all four tie-wings of the ceramic brackets. Very slow (0.05 mm/min) loading was performed until tie-wing or bulk fracture of the bracket occurred. The zirconia brackets did not experience any tie-wing fractures, but instead underwent visually perceptible deformation prior to bulk fracture. The value of compressive force at fracture was adjusted to give the nominal force applied per tie-wing, by observing whether fractures involved one or two tie-wings. A difference of nearly 10 kg was found between the lower force required to induce fracture of a single tie-wing on the single-crystal alumina bracket and the higher force required for one brand of polycrystalline alumina bracket. However, the estimated load to cause fracture of a single tie-wing was similar for the single-crystal alumina bracket and a second brand of polycrystalline alumina bracket. Differences in the fracture loads may arise from variations in the bracket designs, as well as the microstructures of the brackets.

Research using FEA has indicated that an abrupt geometry for the bracket design results in high stresses during loading. Brackets possessing an isthmus connecting the tie-wings demonstrated better stress tolerance than those without this feature.

Wettability and Potential for Plaque Accumulation

The potential of bracket materials to promote microbial colonization, thus inducing plaque formation and potentially caries in orthodontic patients, has been considered in Chapter 6. The critical surface tension (γ_c) of the substrate is considered a key factor in modulating the attraction of species on the surface. Critical surface tension may be defined as the maximum surface tension of a liquid that will form a zero contact angle on a solid substrate. A study by Eliades *et al* that was previously discussed in Chapter 1 evaluated γ_c for samples of the raw materials used for bracket manufacturing, where a protocol developed through the pioneering work of Glantz was utilized. The results indicated a higher potential for increased plaque-retaining capacity for stainless steel brackets, compared to polycrystalline alumina and fiber-reinforced polycarbonate brackets (Fig. 7.15). The total work of adhesion and its polar and nonpolar components were consistent with the critical surface tension ranking, while the nonpolar work of adhesion was higher than the polar component for all three raw materials investigated.

This finding implies a possible higher prevalence of attachment for microorganisms that use dispersive forces, such as van der Waals forces (Chapter 1), as the predominant attachment mechanism to surfaces. However, wetting of surfaces may be governed by hydrophilic interactions and nonpolar Debye forces, Keesom electromagnetic interactions, and London dispersive forces. The complex nature of the oral environment, along with notable lack of correspondence of certain *in vivo* and *in vitro* experimental variables, may account for the results of a study by Fournier *et al* (Chapter 6) that did not confirm the findings of the study by Eliades *et al*. These authors immersed orthodontic brackets in *S. mutans* solution labeled with [^3H]thymidine, employing saliva-coated and noncoated surfaces, and observed decreased affinity of *S. mutans* for all saliva-coated surfaces. Further research is needed to elucidate the complex surface phenomena occurring on orthodontic materials exposed to microbial colonization *in vivo*.

Bracket Slot-Archwire Friction

The slot size and composition are critical elements for the clinical performance of the bracket. While the slot size and the angular offset in the three xyz coordinate planes are highly important parameters affecting the control of tooth movement, the slot surface is also involved in complex sliding friction phenomena with the engaged archwire. Much of the significant research in this area has been performed by Kusy and his colleagues.

Scientific publications on archwire-bracket friction generally concur that metallic slots in contact with stainless steel archwires experience the least friction, while ceramic slots in contact with nickel-titanium and β -titanium archwires experience the greatest friction. Although some authors reported decreased friction for zirconia brackets, others found no differences in friction when zirconia brackets and several polycrystalline alumina brackets were compared. The origin of these observa-

tions lies in the surface roughness of the archwires and bracket slots. Much higher roughness is found for the nickel-titanium and β -titanium archwires, compared to the stainless steel and cobalt-chromium-nickel archwires, as discussed in Chapter 4. The stainless steel slots have lower roughness than the polycrystalline alumina slots, for which SEM observations show that pluck-out of grains occurs during bracket processing. Important variables in the protocols that have been used for investigating archwire-bracket friction are considered in the following sections.

The State

The experimental conditions in reported archwire-bracket friction studies vary from a dry environment to use of water and artificial saliva baths. The results obtained for these different

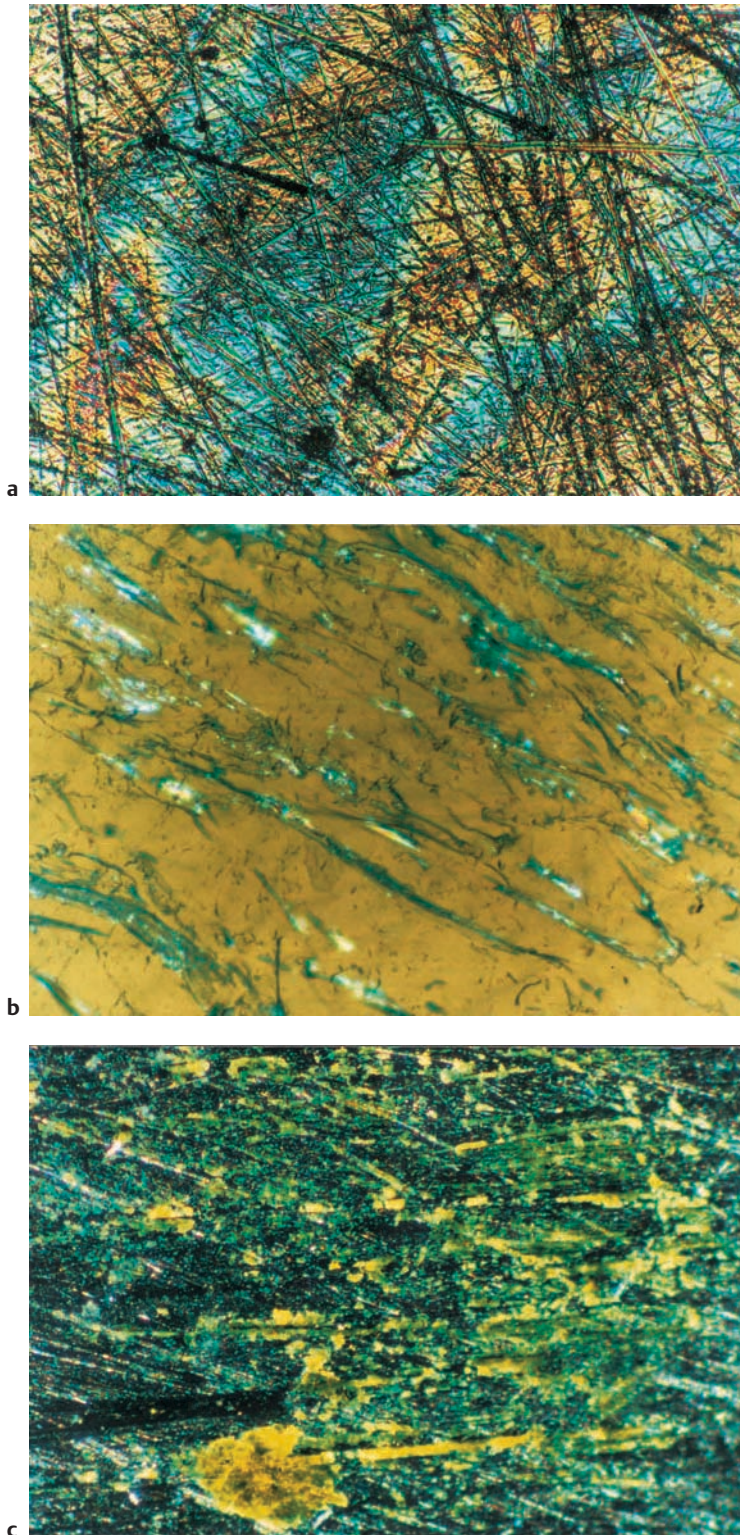


Fig. 7.15 Incident polarized light images of bracket raw material samples placed intra-orally for one hour, illustrating the formation of oral biofilms. Bright-field image, crossed polarizers. Original magnification $\times 50$. (a) Stainless steel. (b) Polycarbonate. (c) Polycrystalline alumina. Note the relatively mature firm developed on stainless steel

conditions present substantial variability. Although in some studies the dry state was found to be associated with increased friction, other studies have reported elevated friction when a liquid interfacial medium was present. The conflicting evidence derived from these studies arises from insufficient knowledge of the rheological and surface properties of the liquid medium; this is an important area for further research.

The formation of oxides on the archwire surface, as a result of exposure to water or artificial saliva, may retard the rate of sliding movement, especially when the relationship between velocity and frictional force (to be discussed later) is considered. Some investigators have conjectured an adhesive behavior of saliva to explain the consistently increased friction noted in the presence of a wet environment. Evidence from retrieval analyses emphasizing the important role of the intraoral pH on the corrosion of orthodontic wires supports this association. In contrast to investigations that showed an increase in frictional resistance when an artificial saliva or human saliva medium was used, studies have also demonstrated that the presence of saliva reduced friction.

Kusy and Whitley have investigated the role of a critical contact angle (θ_c) for sliding mechanics. (This contact angle is between two solid materials, the archwire and bracket slot, in contrast to the conventional contact angle between a liquid droplet and a solid substrate that was discussed in Chapter 1.) Below θ_c , sliding mechanics follows the classical laws of friction, whereas binding and notching increasingly restrict sliding as the contact angle exceeds θ_c . Nonetheless, it is noted that sliding mechanics should only be initiated after the contact angle approaches θ_c for the particular archwire-bracket combination. A theoretical investigation of numerous combinations indicated that the maximum θ_c is less than about 5° , and experimental measurements of the sliding resistance at different contact angles verified the theoretical analysis. These results have potential clinical significance because the orthodontic treatment time can be decreased, since over-alignment of the teeth is unnecessary prior to initiating sliding mechanics. The authors emphasize that accurate calculation of θ_c depends upon having the exact wire and bracket dimensions on the packaging.

Experimental Approaches and Instrumentation

In general, methods employed for the quantitative determination of friction may be classified in two categories:

- Measurement of the roughness of stainless steel, ceramic, or plastic bracket slot surfaces, complemented by morphological study of the wire surfaces prior to and following sliding on the bracket surface
- Actual simulation of sliding at a given, yet arbitrarily defined, movement rate for a specific distance with the use of a mechanical testing machine or custom-made assemblies, under various bracket-wire engagement modes

The first category involves the use of scanning electron microscopy or laser specular reflectance spectrometry. Despite the accuracy and sensitivity furnished by these analytical techniques, the study of the surface profile is limited to a relatively small area examined. Microscopic techniques generally lack a quantification scale to facilitate estimation of surface roughness, which imposes a barrier to elucidating the variability of friction relative to the surface smoothness. Moreover, several studies have supported the lack of a relationship between the surface texture and frictional forces, thereby revealing the presence of unanticipated interactions among the variables involved in this complex phenomenon.

The second category contains flaws in the methodologies that have been employed to simulate clinical conditions, which appear to render its use invalid. The rate of sliding movement has been typically chosen arbitrarily, resulting in a non-standardized parameter that makes comparison of the results from different studies impossible. Nonetheless, when a standard rate is chosen, fundamental discrepancies arise between the clinical situation and the research environment. As Reitan has shown in his pioneering work, the plot of tooth movement (millimeters) as a function of time (days) is a highly individualized, complex curve that is generally characterized by a wide plateau at 15–30 days, followed by a peak at 35–40 days. Therefore the use of movement rates described by simple first-order kinetics is inappropriate.

Kusy and his colleagues have noted a dependence of friction on the velocity at which the surfaces slide past each other. This observation appears to contradict the elementary laws of friction, whereby frictional forces depend only on the vertical component of the applied force, the properties of the surface involved, and the medium in contact with the moving element. To resolve this contradiction, they postulated a dynamic relationship between the formation and detachment of oxides during movement, arising from the wear of the opposing surfaces involved. Hence, at low sliding velocity the formation of oxides prevails and, as a result, the friction increases with time. When the sliding velocity exceeds a critical value, the detachment of oxides from the surface per time unit surpasses the rate of formation, leading to a decrease in friction. The fact that decreased friction has been associated with an increased number of sliding repetitions for the same specimens strongly supports the validity of the proposed hypothesis. Observations of the structure and morphology of retrieved NiTi archwires, indicating the presence of adsorbed KCl crystals and prominent island-like formations arising from the dissolution of nickel, further substantiate the model suggested by Kusy and his colleagues.

Another inherent flaw associated with the experimental approaches for evaluation of friction is the measurement of force magnitude

over some specified distance, presumably to derive information about the extent of the obstacles to movement. An alternative strategy would be to determine the energy dissipated during the movement under the conditions studied. The magnitude of force does not remain constant over the distance set in these experiments, and it is difficult to measure the fluctuations in force during the periods of time involved. Therefore, the rate of sliding movement is technically accelerated to facilitate the extrapolation of force values. The complexity of this issue is further increased when the interference of any force decay occurring in the applied load is considered. Application of retracting forces with the use of elastomeric modular chains is associated with force relaxation that occurs at a varying extent, as discussed in Chapter 8. This degradation may reach levels of up to 60% during the first 24 hours. Thus, the bracket-wire biomechanical model constructed *in vitro* is far from simulating the clinical analogue.

In addition, the majority of the published reports do not consider the bracket-wire “play.” The difference between the nominal prescribed torque and the effective torque for an archwire-bracket combination can be as large as 10°, depending upon the dimensional relationships for the archwire cross section and bracket slot width. Manufacturers intentionally produce archwires with smaller than

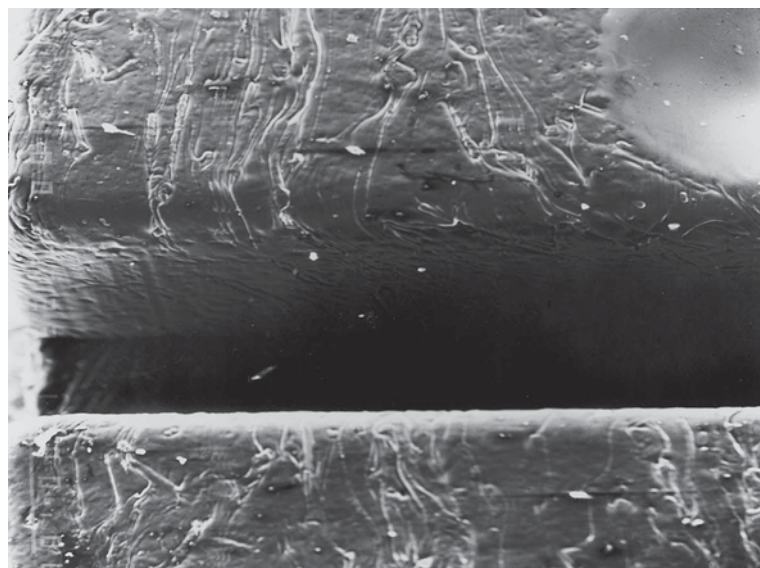


Fig. 7.16 Secondary electron image of a slot, illustrating the presence of rounded edges to facilitate easy insertion of archwires. Original magnification $\times 40$

nominal cross-section dimensions and slot widths greater than the nominal value so as to ensure the full engagement of the archwire in the bracket slot; typically the discrepancies are about 0.013 mm (0.0005 inch). Also, rounded slot edges are usually employed to eliminate such effects and allow for easy insertion of an archwire (Fig. 7.16). While some investigators have observed an adverse effect of predetermined inclination variants on the rate of simulated tooth movement, other investigators have found that the relative dimensions of the bracket slot and archwire cross section have no effect on friction.

In most studies where the β -titanium, nickel-titanium, stainless steel, and cobalt-chromium-nickel archwires were compared, the lowest values of friction were observed for the stainless steel and cobalt-chromium-nickel alloys. However, in some investigations with nominally identical research protocols, stainless steel archwires coupled to stainless steel brackets displayed higher friction than β -titanium archwires in the wet state, while multistrand wires consistently exhibited lower friction than single-strand archwires. Further study is required to explain the surprising behavior of the stainless steel and β -titanium archwires in these experiments.

The Ligation

Elastomeric modules, stainless steel ligature wires, and Teflon-coated ligatures have been used to ligate the archwire to the bracket in friction research. The problem with the use of an elastomeric module ring arises from the force relaxation in these polyurethane polymers, which is discussed in Chapter 8. The force relaxation patterns of the elastomeric module products can vary significantly, with the consensus being that the 24-hour force loss may exceed 40% under laboratory conditions. Significant additional force loss is expected in the oral environment owing to complex surface adsorption phenomena. The oral environment represents much more severe conditions than the dry or artificial saliva environments that have been used for *in vitro* studies. Typical clinical usage occurs over a longer time than represented by the laboratory studies, and there are the complicating factors of enzymatic activity, plaque accumulation, and temperature fluctu-

ations, as well as increased concentrations of oral microbiota induced by the placement of appliances.

The use of stainless steel ligature ties has been shown to increase friction through a dual mechanism. There is a higher engagement force between the archwire and bracket, and additional friction is generated by the contact of the ligature surface with the archwire; however, elastomeric ligatures can induce the same effects. The major problem is the lack of a reliable means to maintain accuracy and reproducibility in the ligation force; the resulting variability in experimental data is generally too great to determine statistical significance between sample groups. The use of a standard number of twisting cycles for the ligature wires in some studies still does not provide the ability to generate a known constant ligation force. Thus, the information obtained from such studies should be considered somewhat subjective. A practical conclusion from these studies was that self-ligating brackets showed less frictional forces, while the figure-of-eight ligature configuration increased friction significantly.

The Clinical Significance

On a clinical level, the relationship of wire surface roughness to sliding friction has not been unequivocally defined. As previously noted, the majority of *in vitro* studies examining this issue have shown that friction increases with increased roughness of the wire and bracket surfaces. Those studies indicated that, in general, the β -titanium and nickel-titanium archwires and the ceramic brackets present increased friction, owing to their roughened surfaces arising from the manufacturing process. However, Kusy and Whitley have proposed that friction is independent of wire roughness. These authors measured the coefficients of friction of orthodontic archwires with RMS (root mean square) surface roughness ranging from 0.04 μm (stainless steel) to 0.23 μm (nickel-titanium) on stainless steel and polycrystalline alumina flats of 0.03 μm and 0.26 μm roughness, respectively. The results showed that the β -titanium wire (RMS surface roughness = 0.14 μm) exhibited the highest coefficient of friction, although the nickel-titanium wire was the roughest. The authors reported mass transfer from the β -tita-

nium wire to the stainless steel and polycrystalline alumina contact flats, which implies that the lower yield strength of the β -titanium wire might have been a major factor for the observed mass transfer. The coefficient of friction should depend upon the roughness of both surfaces in sliding contact, as well as the yield strength and any surface interactions of both materials. Further research is needed to investigate the role of surface roughness on friction, where the roughness, mechanical properties, and surface properties of the materials in sliding contact can be controlled during experiments to yield unambiguous results.

Caution must be exercised when attempting to extend the results of the *in vitro* research by Kusy and Whitley, as well as other investigators, to clinical conditions. Laboratory studies that use relatively clean sample surfaces do not simulate conditions in the oral environment where biofilms and calcified regions are present. Biofilms may reduce the coefficient of friction by producing a boundary lubrication effect through salivary protein adsorption and plaque accumulation (Fig. 7.17). In contrast, the surface roughness and resistance to shear forces are expected to be increased at calcified regions (Figs. 7.18 and 7.19).

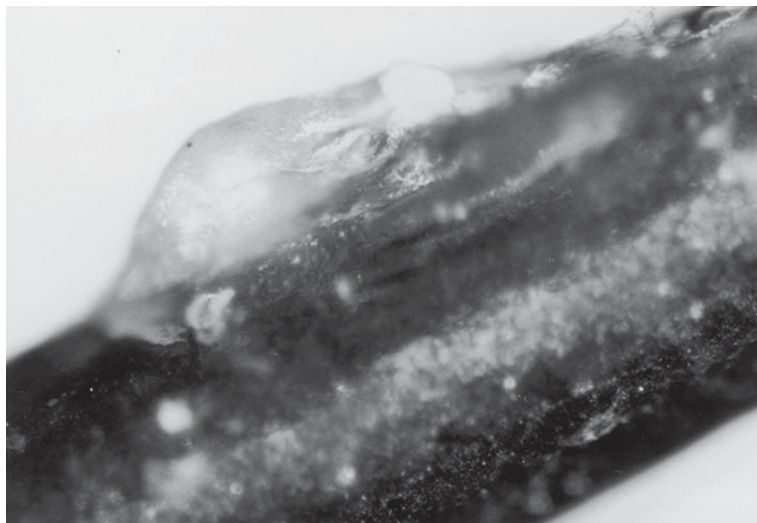


Fig. 7.17 Incident light image of a retrieved NiTi archwire following one month *in vivo*. Note an amorphous solid integument attached on the wire surface. Bright-field image. Original magnification $\times 50$

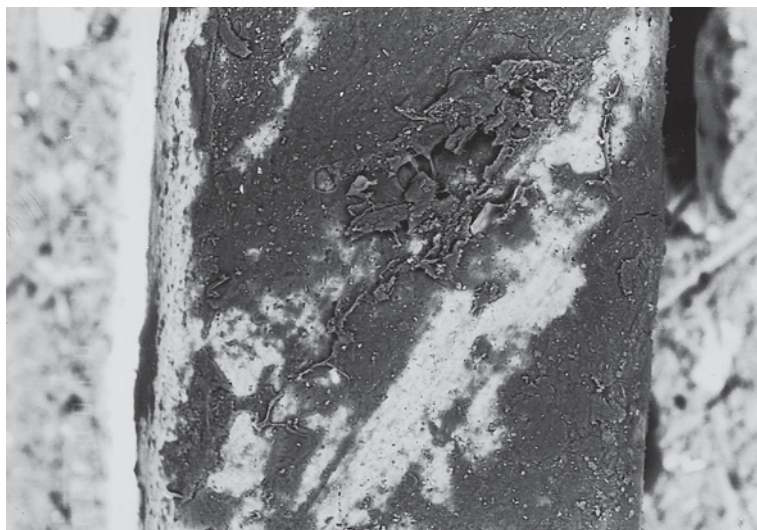


Fig. 7.18 Compositional backscattered electron image of a retrieved NiTi archwire specimen after six months intraoral exposure, demonstrating amorphous film precipitation with numerous granular microstructures of mineralized regions. Original magnification $\times 400$

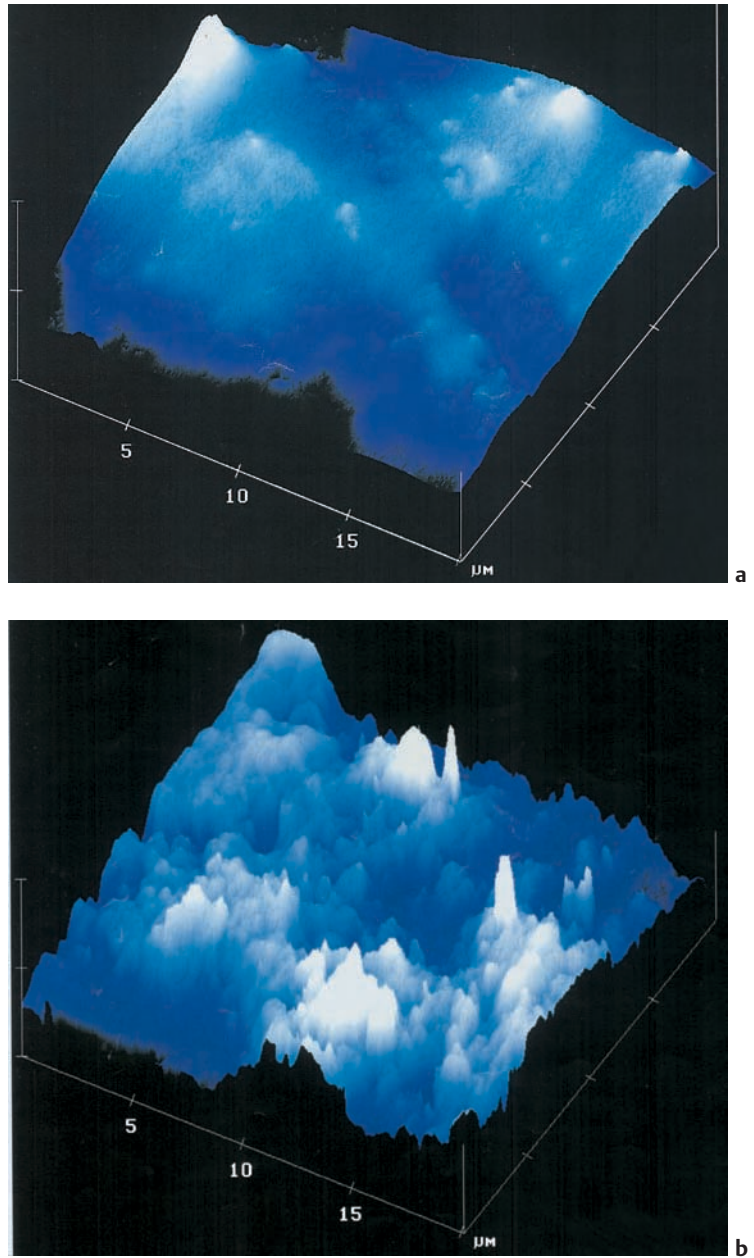


Fig. 7.19 Tapping-mode three-dimensional atomic force microscopic images of NiTi archwires (x and y directions, $5\text{ }\mu\text{m/division}$; z direction, $0.75\text{ }\mu\text{m/div}$). (a) As-received. (b) Retrieved after six months' intraoral exposure. Note the rough topography of the retrieved wire (Courtesy of Dr. Nick Silikas, University of Manchester, U.K.)

The foregoing considerations may explain the results of a study investigating the effect of various archwires on the rate of space closure *in vivo*. As discussed in Chapter 4, this study showed that there was no significant difference for the rates of average space closure *in vivo* between conventional and ion-implanted β -titanium wires. Moreover,

the observed rate of closure obtained with the β -titanium archwires was similar to the rate reported with the use of stainless steel archwires. Further studies are needed to resolve the complex relationships between surface roughness, archwire-bracket friction, and the rate of space closure under clinical conditions.

Debonding Brackets

Debonding of metallic brackets has been the subject of limited research that focused more on the remnant adhesive than the bracket detachment methods. With the advent of ceramic brackets, however, the emphasis was placed on the initial breakage of the adhesive bond without creating enamel damage or leaving fractured bracket fragments bonded to the enamel.

As noted earlier in this chapter, the polycarbonate brackets may peel off, mimicking the debonding patterns of metallic brackets, and therefore their debonding is relatively risk-free. Clinically debonded polycarbonate brackets can exhibit stress-induced bending phenomena, as evidenced from their macroscopic and microscopic features identified in Figure 7.5. The load applied by the pliers to the tie-wing caused a localized concentration of stress and structural changes in the bracket because of the low elastic modulus and strength of the bracket material. Moreover, a fraction of the applied load may be consumed by bending of the flexible base or tie-wing of the bracket.

The initial suggestion of ceramic bracket manufacturers to use the special pliers accompanying the product was subsequently replaced by a plethora of instruments, tools, methods, and procedures advertised to reliably and safely debond the bracket. The proposed methods ranged from special apparatus marketed by the major manufacturers to technical innovations reported by clinicians. In general, abrupt forces occurring accidentally during mastication may impose a greater risk for enamel damage than direct loads applied in the bracket-adhesive complex during debonding.

Early attempts involved the approach of using a device to thermally degrade the adhesive, thereby facilitating easy debonding. Initial concerns about the effect of the resulting elevated temperatures on tooth vitality were not warranted, since the rate of heat transfer is not threatening to the dental pulp and can be manipulated to minimize any adverse effects. Thus, although sequential thermal debonding and cooling of teeth should be avoided, the clinician is advised to apply the procedure for 5-minute intervals, in case the bracket does

not debond during the first cycle of this method.

Ultrasonic debonding has also been attempted and has shown good clinical results. The method involves the application of high-frequency vibrations to disturb the integrity of the complex interfacial structure between the adhesive and bracket base. Fracture of the adhesive-covered protruding formations on the base may occur, along with fatigue failure of the adhesive.

Some authors have proposed notching the underlying adhesive layer with a dental bur as a pre-debonding technique. Thus, a less stable interface is created that will presumably facilitate safer debonding. Confirmation of the validity of this approach, however, requires further research. Other investigators have proposed the use of laser energy to degrade the underlying adhesive layer and facilitate easy debonding. Lasers have been tried in both acid-etching and debonding of brackets, with promising results. This approach has been shown to be efficient for debonding, resulting in a decreased Adhesive Remnant Index (ARI) and a relatively small increase in the pulp temperature. In particular, application of Nd:YAG and CO₂ lasers has shown satisfying results and minimal side effects from increases in the pulp temperature. However, the use of such methods necessitates significant additional cost related to purchasing the apparatus and additional time requirements for including this treatment modality in clinical practice.

Despite the wide array of methods proposed for debonding, it appears that potential problems have now largely been overcome by the introduction of brackets that have clinically adequate, but not excessive, values of bond strength. Much of the turmoil in the orthodontic materials literature over the past two decades regarding the debonding of aesthetic brackets could have been avoided by appropriate testing procedures prior to product release.

Lingual Brackets

The increased interest in aesthetics by orthodontic patients, particularly some adults, has stimulated the introduction of new techniques employing basically the same materials as used in conventional orthodontic therapy, but now placed on lingual enamel surfaces. Modified brackets bonded to the lingual surfaces of the teeth have gained interest. Even though the treatment mechanics involved in lingual orthodontics differs from the mechanotherapy asso-

ciated with the use of standard labial brackets, the materials science principles involved are identical in both techniques. No information is currently available on details of this system from a materials science perspective. However, research has established that no differences exist between the lingual and labial surfaces of the human enamel with respect to the enamel structure and corresponding bond strength values.

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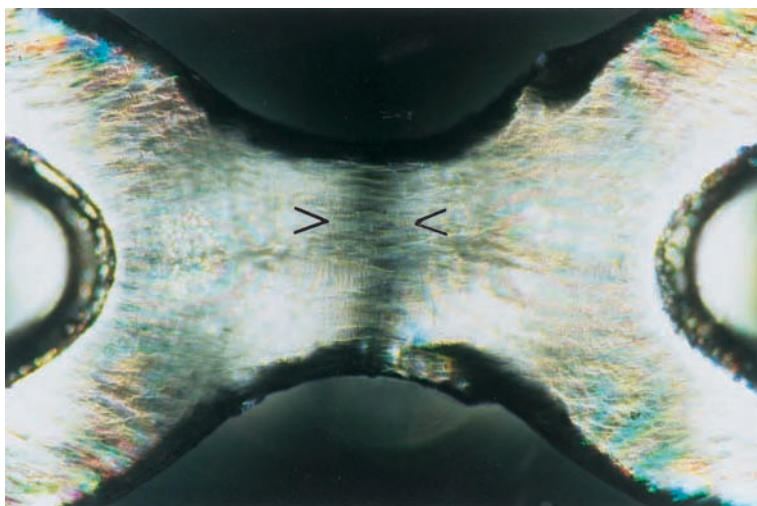
8 Elastomeric Ligatures and Chains

Theodore Eliades

George Eliades

David C. Watts

William A. Brantley



Bright-field double-transmittance polarized-light images of a chain that had been elongated 50 % for 24 hours. (Original magnification $\times 12.5$)

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Introduction

Elastomeric products are used in orthodontics as ligatures and as continuous modules (chains) for the engagement and retraction of teeth. (The use of the popular elastomeric alginate impression materials in orthodontics will be discussed in Chapter 12.) The elastomeric modules were first introduced to orthodontics nearly three decades ago and have gained almost universal acceptance by the profession. They have replaced the elastic appliances used for the retraction of teeth that were fabricated from latex rubber and required daily replacement by the patient. Moreover, orthodontists prefer use of the elastomeric ligatures rather than stainless steel ligature wires.

Despite this popularity, there has been some concern about the force degradation exhibited by the elastomeric chains, which will be dis-

cussed later in this chapter. Because of this concern, over the past decade there has been increasing interest in self-ligating brackets to minimize the inventory required for orthodontic practice and to increase the reliability of the archwire-bracket system. Efforts have also been directed to minimization of the plaque-retaining capacity of the elastomeric chains. Fluoride-releasing elastomeric ligatures have been introduced to minimize the risk for demineralization at the enamel margins. Alternatively, novel retracting assemblies have been developed that instead use rare-earth magnets or NiTi coil springs to provide efficient tooth movement with minimum patient monitoring and significantly longer intervals between treatment, compared to those required with the use of conventional elastomeric chains.

Composition and Structure

The elastomeric ligatures and chains are polyurethanes, which are thermosetting polymers possessing a $-(NH)-(C=O)-O-$ structural unit and formed by step-reaction (condensation) polymerization (Chapter 1). Manufacture of the polyurethane elastomers involves several stages. A basic intermediate is first prepared in the form of a low-molecular-weight polymer, usually a polyester or polyether. This intermediate is then reacted with an aromatic diisocyanate to yield a prepolymer. This elastomer is vulcanized through isocyanate groups by reaction with alcohols or glycols. Detailed information about the synthesis, structure and properties of polyurethanes used for biomedical applications can be found in the book by Lambda *et al.*

Polymers possessing rubber-like elasticity (Chapter 1) have long-chain, lightly cross-linked structures. The restoring force leading to this type of elastic behavior is the result of a decrease in entropy associated with the distortion of a macromolecular chain from its most probable conformation. However, the local mobility of the chain segments must be restricted in order for the polymer to return to its original shape, since irreversible movement of chains

past each another will cause permanent deformation of the material. The cross-links between chains must be relatively few to facilitate large extensions with no rupture of primary bonds. The glass transition temperatures (T_g) of industrial and biomedical polyurethanes range from about -50°C to -80°C .

Indirect measurement of the structure and mechanical properties of these polymers provides insight into the loss of force. The glass transition temperature, previously described in Chapter 1, is considered a fundamental property of a polymer and can be measured using thermal analysis techniques. Chapter 3 discussed the use of differential scanning calorimetry (DSC) to determine T_g for a polymer. Knowledge of the value of T_g often leads to plausible inferences about the polymer structure and mechanical behavior. The glass transition occurs over a range of temperatures at which the polymer transforms from a rigid or glassy state to a rubbery state. For convenience, the glass transition temperature is generally defined as the midpoint of this temperature range, for example, the center of the sigmoidal region on the DSC plot (Chapter 3). The difference in energy between the rigid and rubbery states

corresponds to the increased amount of molecular motion experienced by the polymer after undergoing the glass transition. Below the glass transition temperature, the molecular motions are primarily vibrational, permitting little flexibility. Above the glass transition temperature, coordinated molecular motions occur, allowing the material to become rubbery. The higher the glass transition temperature, the more rigid the polymer, and the formation of a more rigid polymer is associated with greater force delivery, in other words with a higher value of elastic modulus.

Different orthodontic materials companies process their polyurethane products in different fashions. The two main methods of processing the modules are injection molding and die stamping. The die-stamped polymers have been found to be more consistent in physical properties. In addition, the polymer structure of the polyurethane modules may differ between companies (Figure 8.1). This is another source of variation in the glass transition temperature between different products, since the glass transition temperature is directly related to polymer structure. The primary structural influences on T_g are the composition, the steric interferences, and the types of bonding present in the molecule. All of these factors influence molecular motion.

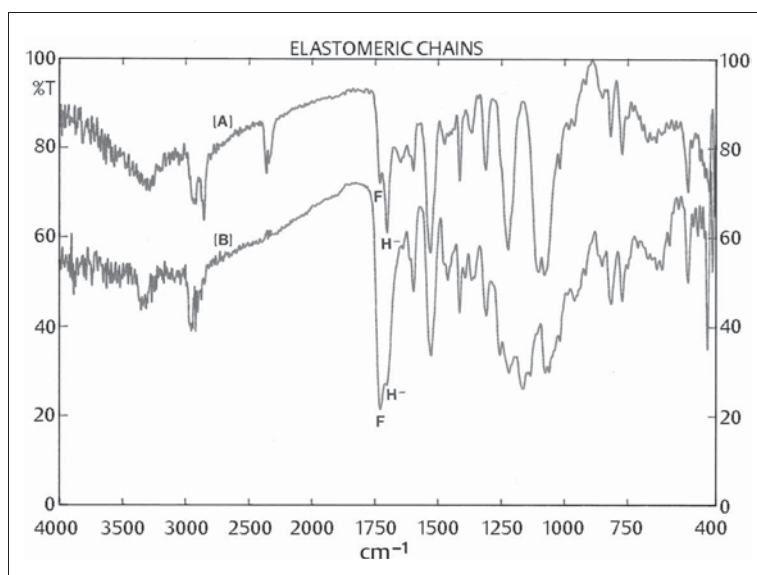
An investigation by Renick and colleagues has shown that glass transition temperatures

can differ among some polyurethane chain products by $15^\circ - 20^\circ\text{C}$, as shown in Figures 8.2 and 8.3, indicating substantial differences in their structure or composition. (These DSC plots can be interpreted by referring to Fig. 3.12.) A higher T_g corresponds to a more rigid polymer, because of either the presence of more cross-linked chains or larger side-chains causing steric interferences. A general graph of the elastic modulus for a polymer as a function of temperature (Fig. 8.4) indicates the existence of a rubbery plateau region following the glass transition. A higher value of T_g may indicate a polymer that is in an earlier stage of the rubbery plateau at room temperature.

Pigmenting these products, which is done by manufacturers to increase patient acceptance, raises the question whether the pigments affect the structure of the elastomers. Certain types of fillers have been incorporated by the polymer industry to provide color. However, the compositions of the orthodontic chains are proprietary information, and information about the pigmentation process is not available. Whether the filler bonds to the polymer remains a question for future research. If the pigment can form cross-links with the polymer, it could potentially raise the glass transition temperature.

The study by Renick and colleagues of as-received products indicated that, while the use of gray, red, and purple pigments had no significant effect on the T_g for two brands, there

Fig. 8.1 Multiple internal reflectance FTIR spectra of two commercially available elastomeric chains [A] and [B], demonstrating different molecular composition and different extent of free (F) (1730 cm^{-1}) vs. hydrogen-bonded (H-) (1730 cm^{-1}) polyurethane carboxyls



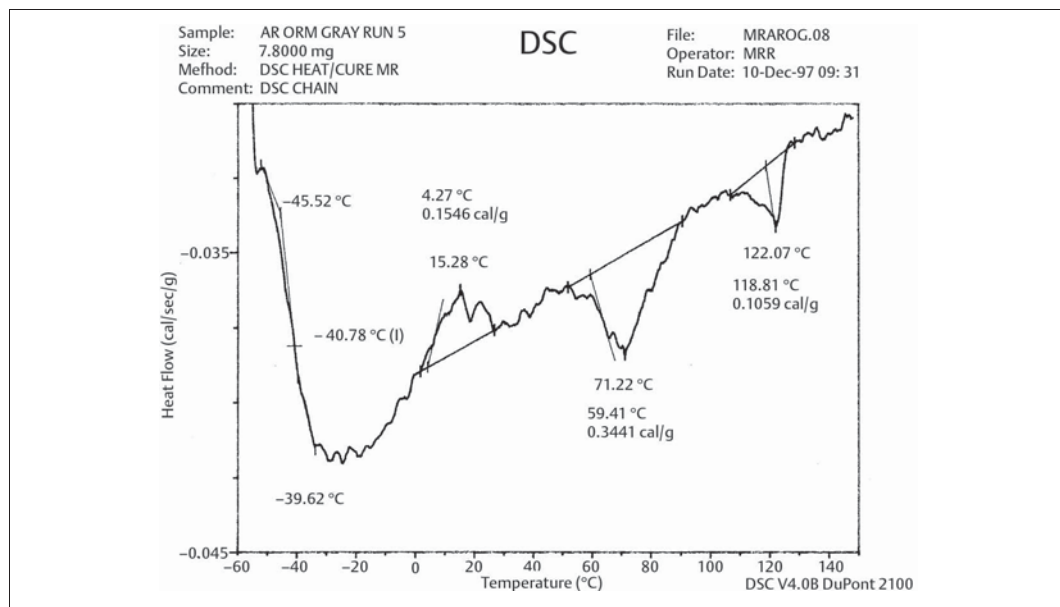


Fig. 8.2 DSC plot for as-received gray-pigmented elastomeric chain manufactured by Ormco. The glass transition temperature is approximately -41°C (From Renick, 1999. An abstract describing this study is found in Renick *et al*, 1999a)

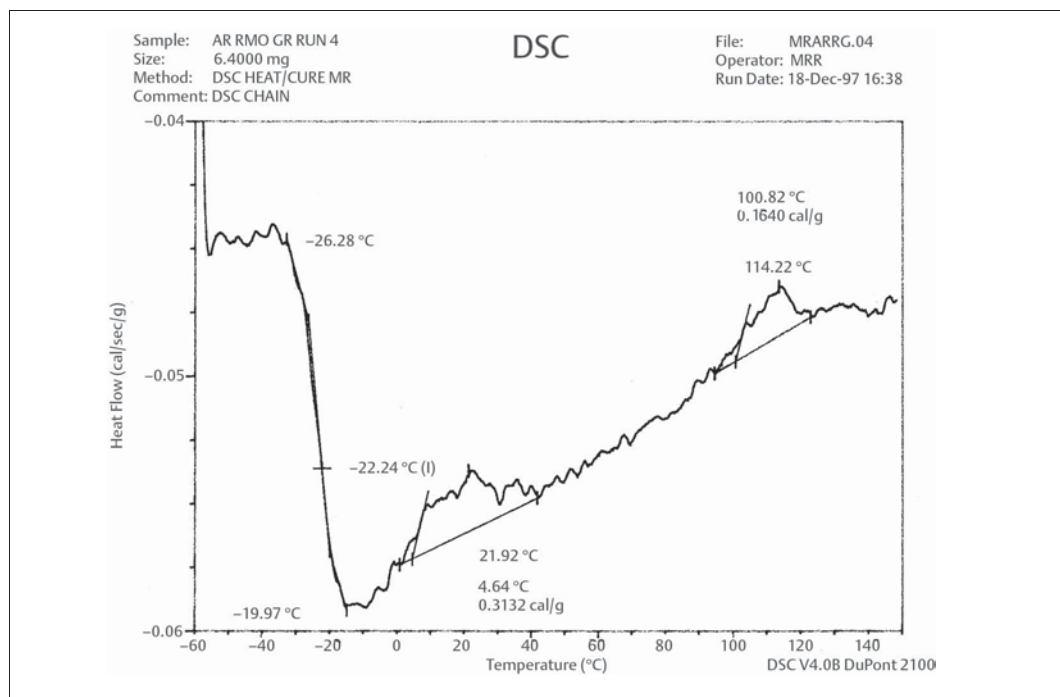


Fig. 8.3 DSC plot for as-received gray-pigmented elastomeric chain manufactured by RMO. The glass transition temperature is approximately -22°C (From Renick, 1999. An abstract describing this study is found in Renick *et al*, 1999a)

was a significant difference in T_g for the gray-pigmented and purple-pigmented chains of the third brand. The DSC plots for specific brand-pigment combinations were similar for the as-received condition and *in vitro* testing in which four-segment modules were stretched for four weeks in air to a length of 2.5 cm, approximating the *in vivo* molar-to-canine distance. The DSC analyses of specimens after four weeks of *in vivo* use in randomly selected patients undergoing orthodontic treatment revealed a second glass transition (Fig. 8.5) that was not present for specimens in the as-received condition or after *in vitro* testing in air. The origin of this peak, which is due to the effects of the oral environment on the polyurethane polymer, is presently unknown. In general, studies focusing on the mechanical characteristics of colored elastomerics have failed to reveal differences between the conventional gray or clear elastomers and their pigmented counterparts.

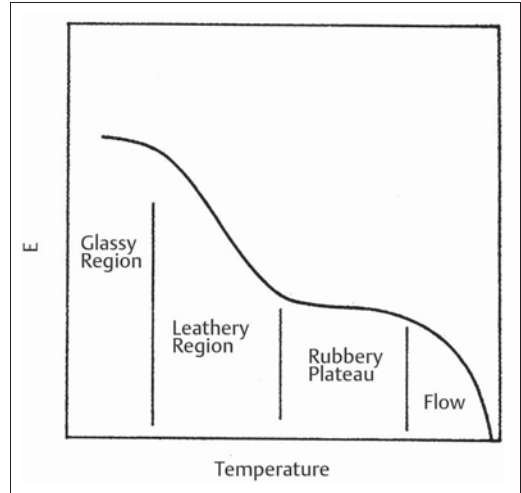


Fig. 8.4 Generalized dependence of the elastic modulus (E) for a polymer upon temperature, showing the trend in values for the different types of structures. (Adapted from Rosen, 1993)

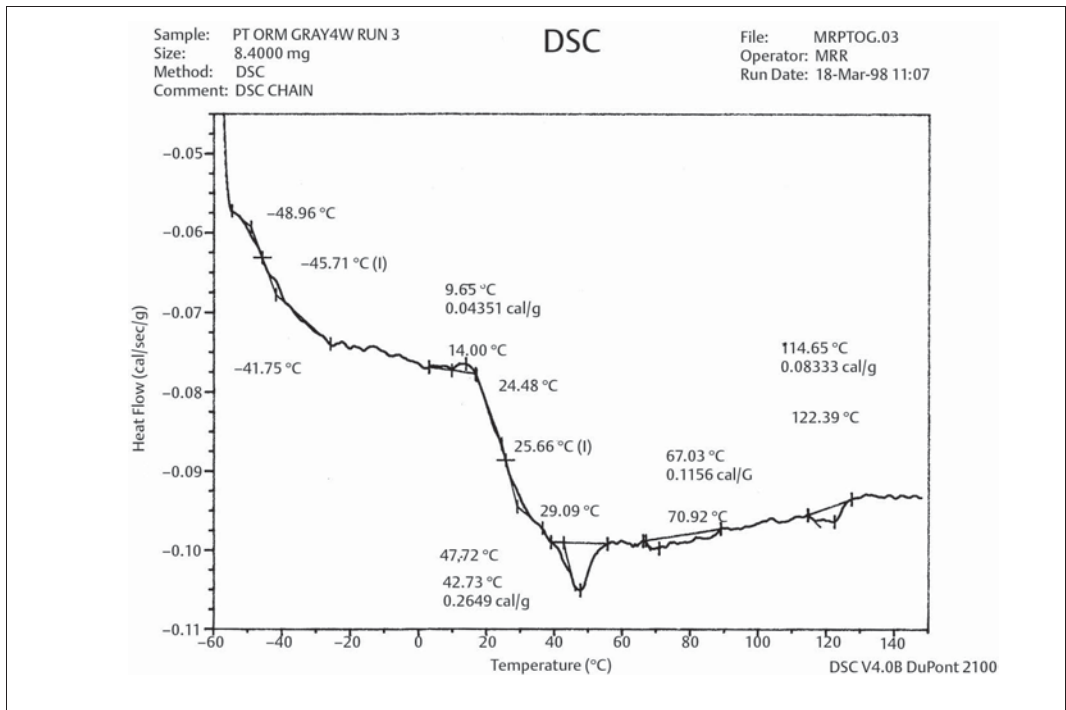


Fig. 8.5 DSC plot for gray-pigmented elastomeric chain manufactured by Ormco, following four weeks of use *in vivo*. Note the second glass transition at approximately 26 °C that is not present in Figure 8.2. (From Renick, 1999. An abstract describing this study is found in Renick *et al*, 1999b)

In addition to its elastic behavior, a stretched elastomeric chain should have relatively high tensile strength and elastic modulus to avoid premature rupture and to provide desired levels of force delivery, respectively. Higher values of these mechanical properties are associated with crystalline polymers where stress is employed to alter the orientation of the molecular arrangements. This effect should also provide some increase in the polymer crystallinity and mechanical properties when the polyurethane chains are stretched. In the unstretched state the elastomeric modules have a more completely amorphous structure. The facility of molecular movement in the polymer structure is evidenced by the value of T_g , which includes the effect of cross-links in limiting the gross mobility of the polymer chains. Another potential method for improving the mechanical properties of these products would be to incorporate fillers in the polymer matrix, in a similar manner to that for composite restorative resins.

Elastomeric Ligatures

Conventional Ligatures

Elastomeric ligatures constitute the major medium engaging the archwire to a bracket slot. The clinician may prefer the use of these materials over the 0.20 mm to 0.36 mm (0.008–0.014 inch) stainless steel ligature wires for several reasons, including their ease of application, patient-friendly nature, aesthetic appearance, potential for fluoride release, and decreased force delivery. This force has been found to reach the levels achieved with stainless steel ligatures in twin brackets where the extension of the elastomer is maximized because of the larger size of the bracket.

Taloumis *et al* have reported the force decay of a variety of elastomeric ligatures in a simulated oral environment. Even though this *ex vivo* environment is expected to be much less severe than the oral cavity, an exponential initial force loss was observed, which reached 50–60% during the first 24-hour interval. The force decrease continued at a significantly lower rate for 7–10 days, and signs of permanent deformation and alteration of the shape of the elastomers were evident following

The general properties of elastomers, which follow from these preceding considerations, have been summarized by Billmeyer:

- When stretched rapidly, elongations greatly in excess of 100% can be achieved, with no major loss of energy.
- The highest values of tensile strength and stiffness are obtained after full stretching.
- Upon removal of the tensile force, a rapid contraction occurs, since the polymer structure has a strong tendency to return to its original condition.
- Full recovery takes place as long as the tensile force does not exceed the elastic limit, demonstrating the high resilience of these materials.

The form of the stress-strain curve for an elastomer and the dependence of force delivery and recovery on the rate of loading have been described in Chapter 1.

their recovery from the medium. It was concluded that, while these ligatures appear suitable for use during initial aligning and leveling, their rapid force loss and permanent deformation may preclude use for rotational and torque corrections. The force exerted on the archwire by the elastomeric ligature is expected to depend upon the size and dimensions of the module (as well as upon the bracket design and size). When the overall diameter of the module is decreased for a given mass of elastomer, the force delivery increases because of the greater wall thickness; this anticipated relationship was observed by Taloumis *et al*.

The elastomeric chains have the additional disadvantage of not being inert in the oral environment. Huget *et al* observed that water acts as a plasticizer by weakening intermolecular forces in the polyurethanes, leading to chemical degradation. Chromatographic analysis has shown increased leaching from elastomeric modules immersed in water and subjected to seven days of stretching. The deleterious synergistic effect of loading and water immersion may be attributed to susceptibility to hydrolysis of the ester or ether backbone linkages in the

polyurethanes. The resulting weakening of the elastomer will cause a reduction in the load required to maintain a fixed extension and contribute to the force degradation observed in many studies.

Under clinical conditions, it is highly important that the elastomeric ligature provide sufficient force to maintain full engagement of the archwire within the bracket slot. Extensive research has revealed a large force decay during the first 24 hours after placement of the elastomerics, as will be discussed later in this chapter. The introduction of elastomeric modules with substantially increased total diameter-to-internal diameter ratios (*i.e.*, greater wall thickness), which would be capable of exerting higher forces, might alleviate this problem. Some studies have shown that a higher initial force results in decreased force loss over time, and it might be anticipated that such modules with greater wall thickness might more adequately maintain the force at desired levels for longer periods than will currently available modules. Elastomeric ligatures may be ineffective for treatment applications involving large rotational moments, where the exertion of a substantially decreased force would fail to completely engage the archwire in the bracket slot for the full term of activation. Thus, the use of elastomeric ligatures should be avoided where full-slot engagement is critical for successful application of the chosen mechanotherapeutic approach. Alternatively, stainless steel ligatures may be used on such occasions, or the orthodontist should shorten the time intervals between visits. Other strategies may also be employed to maintain the high force levels, such as use of the “figure 8” configuration to increase the initial force level of the module.

The pH and temperature variations in the oral environment, along with accumulation of plaque and formation of microbial colonies on the surfaces of the elastomerics, may affect the structure, surface properties, and conformation of the polyurethanes. Specimens retrieved after short times following placement in patients undergoing orthodontic treatment have a proteinaceous surface film with minimal evidence of phosphate mineralization. At the end of three weeks there is precipitation of Ca and P, forming calcium phosphates on the surfaces of the retrieved modules. The high pro-

tein content of the biofilm on the surface of these materials, and the calcification pattern observed, are similar to those expected for a nonspecific mechanism of film adsorption on biomaterials exposed to body fluids (Figs. 8.6 to 8.8). The observed substantial degradation in the force delivery of modules aged *in vivo* is thus not surprising.

Fluoride-Releasing Elastomerics

Advances in the field of elastomerics include the introduction of products with fluoride-releasing features. The introduction of a reliable means of long-term fluoride release in the area adjacent to the bracket-adhesive margins would be of paramount significance. Although few studies have focused on the temporal characteristics of this fluoride ion release, the results to date are contradictory. This may be attributed to variations in the experimental protocols followed for the *in vitro* studies. Some authors have provided evidence of the beneficial characteristics of these products, demonstrating that for a period of two weeks the local *Streptococcus mutans* colonies declined and the adjacent enamel microhardness was increased at the 20 μm depth level. Although the rate of elution in one study was found to follow a pattern characterized by a steep decline after three weeks, Wiltshire has reported measurable elution after six months under *in vitro* conditions.

The time dependence of fluoride release from elastomeric ligatures must be examined with different criteria from those used for investigating the fluoride release from adhesive resins or other orthodontic materials for relatively long-term applications. This is because the life expectancy of the elastomerics *in vivo* rarely exceeds the period between consecutive appointments (approximately one month). Frequent changes are required in these products for a variety of reasons, including excessive plaque accumulation, discoloration, the need for reactivation of the desired force level, or insertion of a new wire. Therefore, long-term fluoride ion elution will not be an important factor for a reliable and efficient fluoride-releasing elastomeric carrier.

A critical issue for the clinical applicability of reported fluoride release levels pertains to the

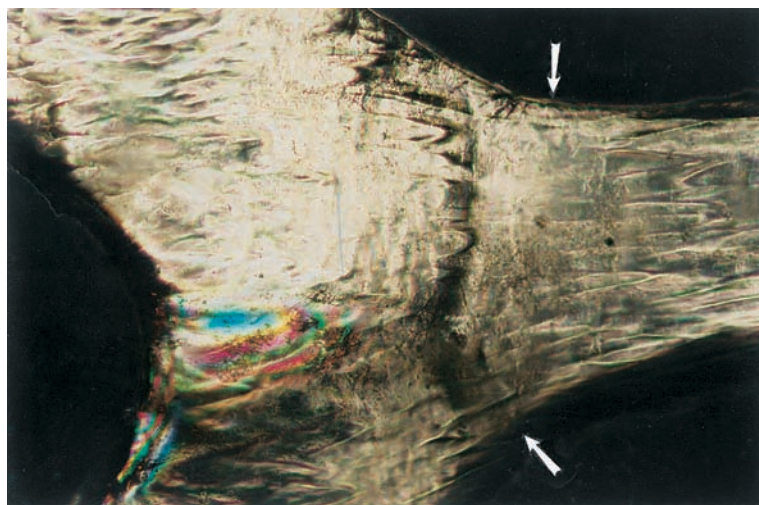
reliability and scientific soundness of the experimental protocols employed. Considering the substantial variation of *in vivo* conditions and the resulting accelerated aging of the elastomeric modules (to be discussed in a later section), *in vitro* methods for investigation of fluoride elution rates must be viewed with skepticism. The complex intraoral phenomena cannot be simulated reliably by the various nonagitated storage media that have been employed in some studies. Consequently, proper investigation of the fluoride release potential and rate requires the use of *in vivo* conditions.

In contrast to the minimal clinical significance of an extended fluoride-release ability for elastomerics, the potential effect of the release process on their mechanical properties is of critical importance. Storie *et al* found that fluoride-releasing elastomerics were unable to deliver force within the optimal range for tooth movement after one week of fixed strain; conventional elastomerics exerted the required force levels for a period of three weeks. The inability to deliver orthodontic force levels was attributed to the effect of fluoride release on the structure of the elastomer. Thus, caution must be exercised regarding the frequency of patient visits and the need for force reactivation when using these products during orthodontic treatment.

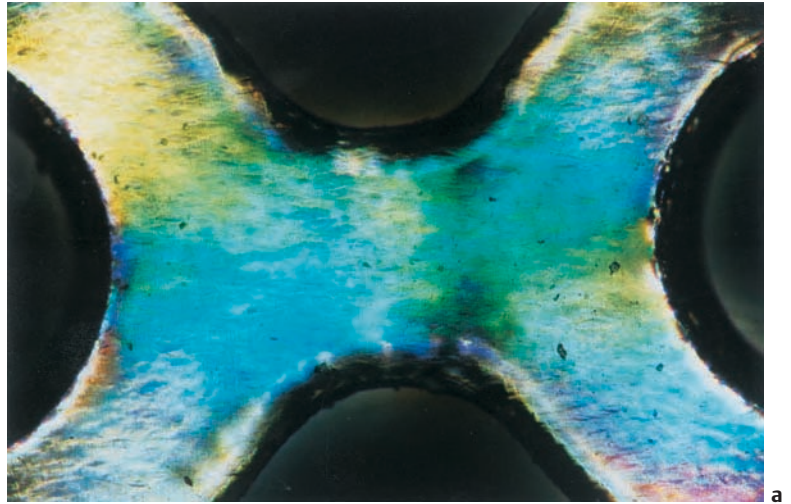


a

Fig. 8.6 Bright-field transmittal-light phase-contrast images of an elastomeric chain after 24 hours of intraoral exposure at approximately 50% elongation. Note the crack propagation at the middle of the inter-molecular link from the marginal site (a) and creep-induced material thinning at the ring-link transitional zone (b). Original magnification $\times 50$. (From Eliades *et al*, 1999)

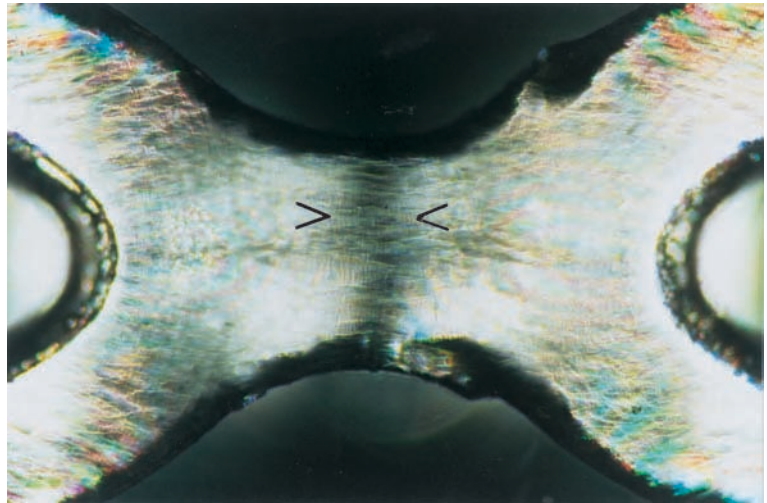


b



a

Fig. 8.7 Bright-field double-transmittance polarized-light images of the reference condition (a) and after recovery (b) for a chain that had been elongated 50% for 24 hours. Note the direction of the isoclinic fringes (dark regions) at the middle of the intermodular link and at the ring-link transitional zone. The structural alteration coaxially to the applied load is very characteristic at the link site. Original magnification $\times 12.5$



b

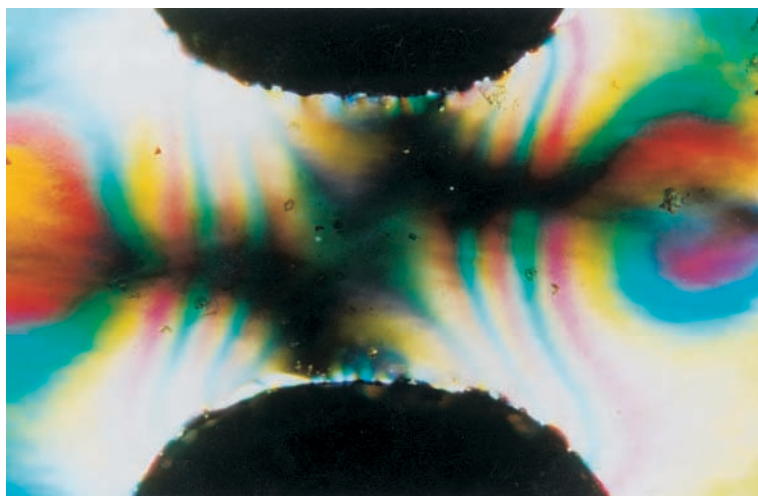


Fig. 8.8 Bright-field transmitted polarized-light image following recovery of a chain that had been elongated 50% for 24 hours. The close arrangement of the isochromatic fringes implies high residual stress intensity and concentration at the intermodular link. The

isoclinic (dark) fringes are related to the stress direction which, although applied coaxially to the chains, is oriented perpendicularly to the link margins. Original magnification $\times 50$. (From Eliades *et al*, 1999)

Elastomeric Chains

In vitro Studies of Force Degradation

The area of elastomeric modules (chains), and especially their force decay, has been studied to a much greater extent than for the elastomeric ligatures. The force relaxation patterns of various commercially available brands have been measured using a variety of test media and experimental configurations. Although most of the elastomeric modules currently available are fabricated from similar raw materials using similar methods, significant differences in their force decay characteristics have been reported. These differences may be attributed to several factors:

- Variations in manufacturing techniques, where die stamping or injection molding is used to fabricate the modules
- Variations in the additives incorporated in the basic polyurethane polymer to obtain the final product
- Variations in morphological (ellipsoid or circular modules) or dimensional characteristics (presence or absence of an intermodular link) of the chains.

The many *in vitro* studies that have measured the force degradation rate of elastomeric modules have employed:

- Dry or wet testing states including water, artificial saliva, or fluoride media, with varying temperatures
- Steady force application or decreasing forces to simulate clinical conditions where tooth movement takes place
- An acidic or neutral pH environment.

The consensus of these studies is that the elastomeric modules experience a steep decline in force, ranging from 40% to 50% during the first 24 hours, which continues at a lower rate for two to three weeks. Ash and Nikolai showed that the force degradation is greater *in vivo* compared to *in vitro* conditions. In early studies, Kovatch *et al* and Brantley *et al* found that a plot of the logarithm of force as a function of the logarithm of time yielded an excellent straight-line fit over normal test periods (four weeks), indicating a power-law relationship between force and time. More recently, Stevenson and Kusy have employed a Maxwell-Weichert model (Chapter I) that fits the force degradation

data for elastomeric modules equally well. This model assumes that the force degradation arises from two processes: a rapid mechanism that is responsible for the large initial force loss and a second mechanism that accounts for the relatively slow rate of force loss at longer periods of time. Further fundamental studies are needed to elucidate the basic mechanisms for the force decay in these elastomerics.

There is clinical concern with the use of elastomeric modules about maintaining force levels within a range suitable to facilitate tooth movement. Traditionally, these modules have been used for the retraction of anterior teeth to close extraction spaces as well as for the closure of diastemas. With the advent of rare-earth magnet assemblies and of superelastic NiTi coil springs that are capable of providing a constant low force over an extended period of time, resulting in increased time intervals between appointments (Chapter 4), the use of elastomerics has diminished significantly. Rotated teeth and interdental spaces usually located in the anterior maxillary and mandibular arch segments represent a challenge for the elastomeric modules, since no other suitable means to direct the force over such wide areas is currently available. There has been criticism related to the lack of mechanical control of teeth engaged in elastomeric chains, because loss of the directional control of moments leads occasionally to undesirable mesiodistal or buccolingual rotations. However, the alternative option of using an elastic thread to achieve the desired

tooth movement presents far more disadvantages.

As previously described, elastomeric chains lose almost half of the applied force very early and continue to relax for an extended period of time. Some investigators have proposed that this deficiency may be counteracted by applying a higher initial force of 3–4 times the desired force level. However, there have been contradictory results from *in vitro* studies of the effect of initial force magnitude on the subsequent rate of force decay. More importantly, the application of an orthodontic force up to four times the optimum level for tooth movement may have unpredictable outcomes on biological processes. Although it is doubtful that such high forces applied to the tissues for only a few hours may cause hyalinization, there is no evidence on this issue, and therefore the proper approach is to avoid any likelihood of harming the patient.

Several studies have also dealt with the use of prestretching to eliminate the force loss by the elastomeric modules. Two modes of prestretching have been proposed; the instantaneous prestretching technique used by Young and Sandrik and by Chang would be much more convenient for the orthodontist than the extended-time technique of prestretching described by Brantley *et al.* While some reports have been optimistic about the effectiveness of prestretching, evidence has also been presented that this treatment eliminates only about 10% of the decrease in force decay.

In vivo Aging Phenomena

Research on the effect of the oral environment on the structural conformation of elastomeric modules has shown that the stress absorption mechanism in these materials seems to be that of macromolecular chain orientation and elongation, coaxially to the applied load (Figs 8.9 and 8.10). However, regional discontinuities emanating from the design of the chains may locally exaggerate stress effects, leading to a micro-tearing pattern and establishment of micro-fractures that propagate from margins to bulk material, as illustrated in Figure 8.6 (a) and (b). This failure pattern involves fracture lines directed perpendicular to the elastomeric margins, following the residual

stress vectors, as demonstrated from the direction of the isoclinic fringes in polarized light images shown in Figure 8.7 (a) and (b).

The characteristic pattern of fringe formation in the polarized-light microscopic examination of these materials is the result of alteration of the polarized light by the residual internal stresses into two waves that travel at different velocities (Fig. 8.8). This phenomenon allows estimation of the strain intensity and direction developed in the material. In the elastomeric chains possessing well-differentiated intermodular links (*i.e.*, open chains), the direction and intensity of the residual strain correspond to the link extension pattern. This is in contrast

to closed elastomeric modules, for which the strain developed in the modular rings was found to be much higher. Moreover, as the rings are subjected to additional stresses arising from the engagement of the module into the brackets, a higher tendency for force degradation or ring failure is anticipated in the closed elastomeric modules.

Significant changes in composition of elastomeric modules aged *in vivo* have been described by Eliades *et al.* After an exposure of 24 hours, the surfaces of the modules were covered by a non-continuous proteinaceous film that was rich in alcohol groups and with

minimal evidence of potassium and sodium mineralization. Following three weeks of intraoral exposure, the surfaces were covered by well-mineralized proteinaceous films composed of calcium phosphates with carbonate and acid-phosphate impurities (Figure 8.9). This pattern of precipitation appeared to dominate the surface, regardless of the specific brand or type of chain. X-ray microanalysis of regions demonstrating low-atomic-number contrast showed an almost uniform distribution of K, Na, Cl, and S, while high-atomic-number contrast regions were mainly composed of Ca and P. It seems that protein adsorption on

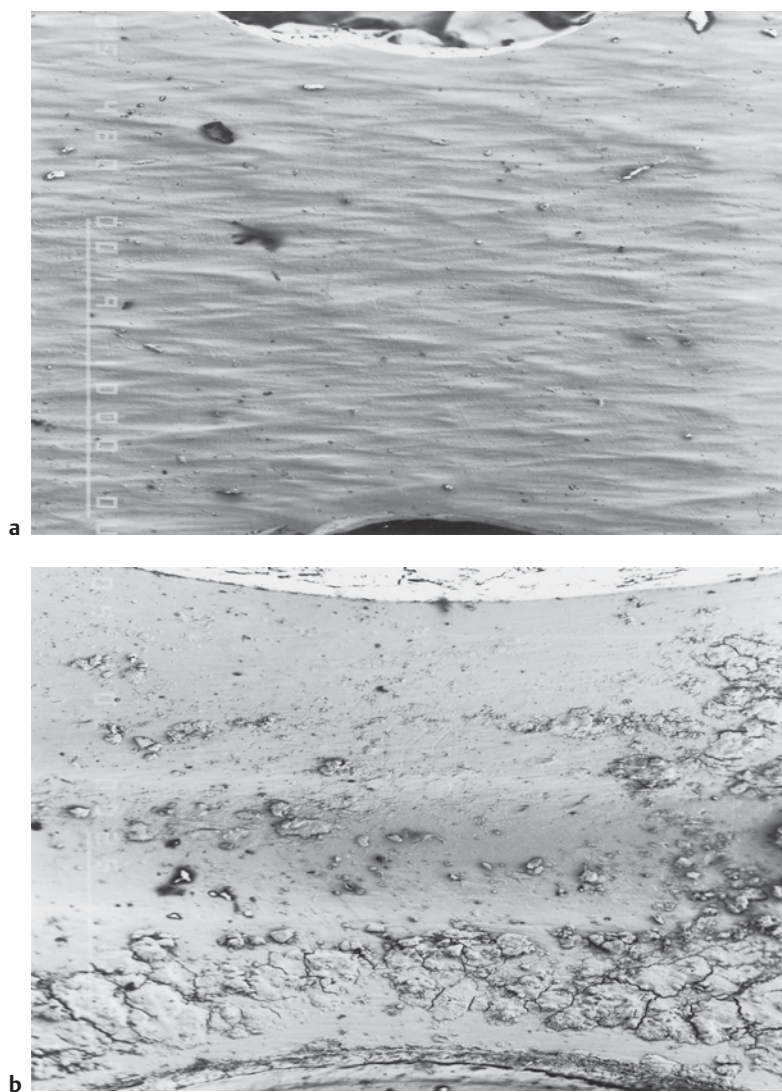


Fig. 8.9 Secondary electron images of an intermolecular link of a chain before (a) and after (b) three weeks of intraoral exposure. Note the orientation and arrangement of the mineralized precipitates. Original magnification $\times 40$

elastomeric surfaces induces entropically favorable conformational changes that, at an early stage and under localized conditions, may act as nuclei for the formation of microcrystalline deposits from Na, K, and Cl, which are present in abundance in the oral environment. These deposits may dissolve under pH fluctuations that facilitate macromolecular displacement reactions, thereby altering the pattern of the developing adsorption process. On mature specimens where calcium precipitation is initiated, the size and valence of the calcium atoms appear to stabilize the structure by the formation of calcium phosphates under ordinary condi-

tions. The effects that the oral biofilm adsorption and these *in vivo* microcrystalline surface deposits have on the mechanical properties of the elastomeric modules are expected to be relatively severe and to compromise the performance of these modules. Another manifestation of these effects is the second glass transition that has been observed for modules that have been used in the oral environment (Fig. 8.5). Future research should be directed to obtain further understanding of the relationships between these fundamental observations of aging phenomena and the *in vivo* performance of the elastomeric chains.

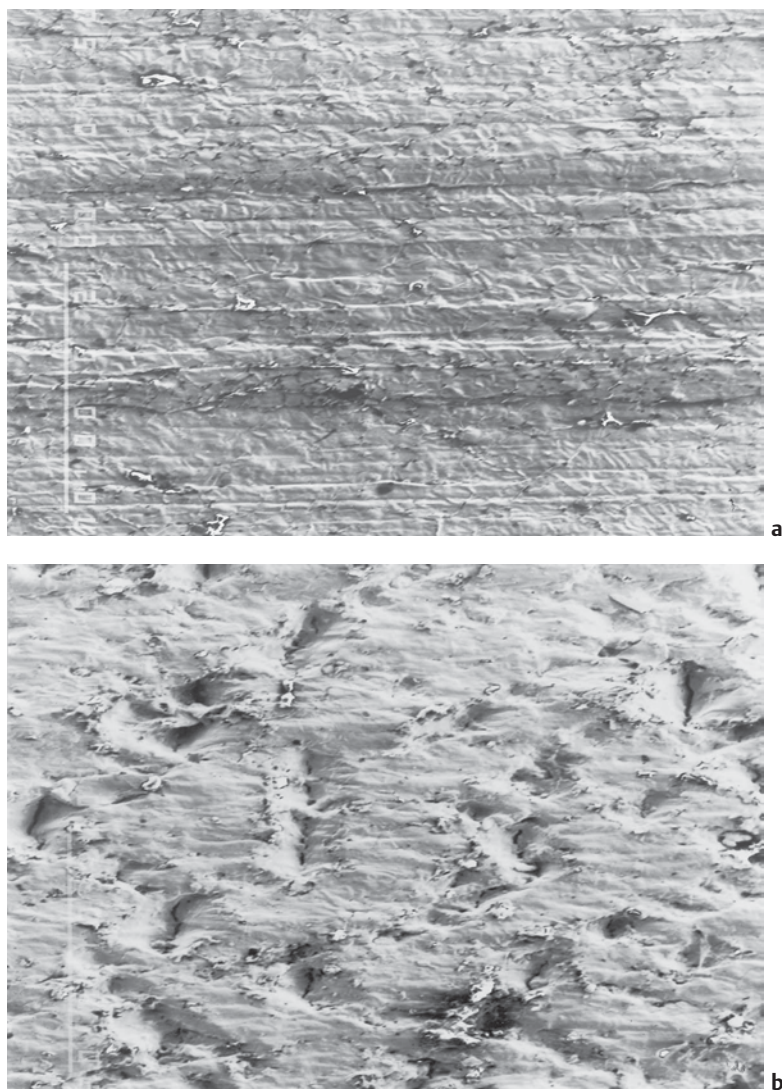


Fig. 8.10 Secondary electron images of an intermodular link of a chain before (a) and after (b) 50% coaxial elongation for 24 hours. Note the changes in the surface morphology of the stressed specimens due to regional failures at a direction vertical to the force applied. These regional failures release considerable amounts of strain energy, allowing for high percentage elongation without complete rupture. Original magnification $\times 450$

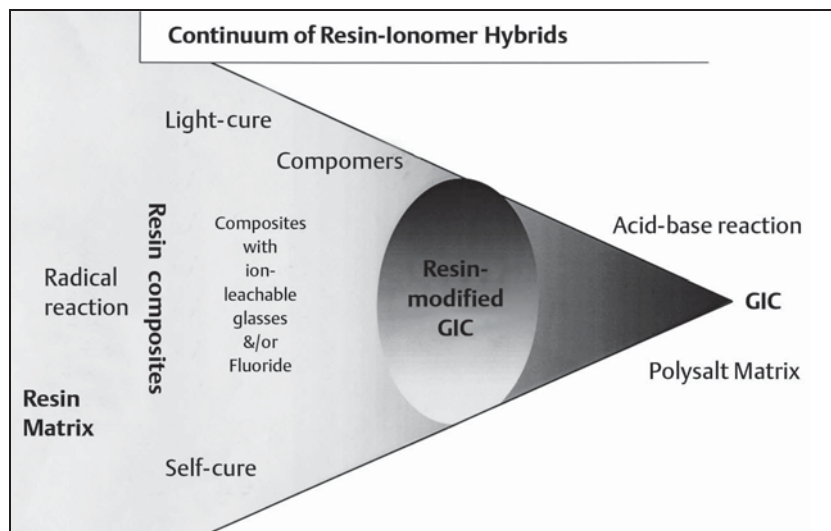
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9 Orthodontic Adhesive Resins and Composites: Principles of Adhesion

David C. Watts



Continuum of resin adhesives that lie between pure resin composites and pure glass-ionomer cements

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Introduction

Adhesive bonding is important for orthodontics, especially in terms of the fixation of brackets to teeth. This situation involves the joining of two solid substrates or adherents by an intervening layer of adhesive agent. The surface interface characteristics are crucial to the success of the bond, as are the inherent properties of the adhesive. Many aspects of the situation are rather general. That is, they are not entirely restricted to the orthodontic context itself.

We shall first sketch sufficient background of adhesive science to facilitate appreciation for the necessary properties of dental orthodontic adhesives. Secondly, we shall outline the range of materials that have been considered for use as orthodontic adhesives. Thirdly, we shall give more detailed treatment of the monomer and monomer-composite systems in extended use. The associated surface modification regimes for the tooth and bracket substrate will briefly be addressed.

The Broad Rationale of Adhesive Science

The characteristic requirements and properties of adhesive agents for orthodontics must be understood in terms of the molecular and structural mechanisms of adhesion. One of the basic questions of physicochemical science is “Why do materials cohere at all?” On the basis of molecular theory, the answer is given in terms of a range of attractive forces that may operate in and between molecules. These may produce bonds of varying *strength* (that is, the energy required for their disruption), ranging from covalent and ionic bonds to hydrogen bonds and other relatively weak intermolecular forces.

There are a few solids that will spontaneously self-cohere when brought into sufficient proximity. Two familiar examples from dentistry are cohesive gold foil and waxes.

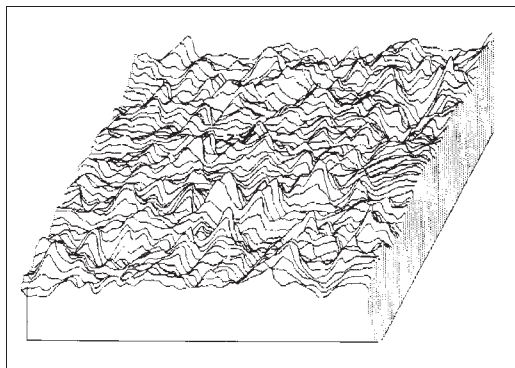


Fig. 9.1 Schematic illustration of the typical microscopically rough nature of solid surfaces that are bonded by adhesives

Both of these materials are sufficiently plastic in deformation as to self-adapt topographically at the molecular interfacial level, though some physical agency is needed to promote this phenomenon: mechanical force upon gold foil, and gentle heat in the case of waxes. Other examples of joining-coherence may arise under more extreme conditions, such as metals at the melting point, as induced in procedures such as welding or brazing.

Most other solids, and certainly tooth tissues and orthodontic brackets, do not cohere upon touching. This is not because of the absence of surface forces but, first, because such forces operate over very small distances and decrease rapidly in magnitude with the inverse sixth or seventh power of separation. Secondly, the solids in question are microscopically rough, as illustrated in Figure 9.1. Hence, when the solids are brought into “contact,” the situation is like two mountain ranges being superimposed *en face* (Fig. 9.2). The points of actual molecular contact are only a few percent of

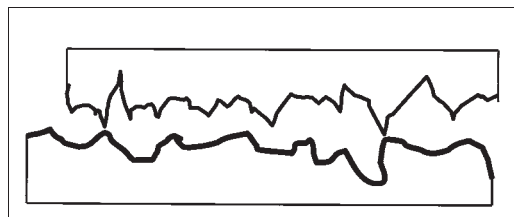


Fig. 9.2 The analogous macroscopic situation to Fig. 9.1 is that of two mountain ranges being forced into contact with each other

the whole area. Since solids such as enamel or metal brackets are stiff and elastic, their surface “mountains” cannot flow to self-establish molecular adhesion.

The empirical solution to this problem has, of course, been known for millennia. A fluid agent must be introduced between the solids in question. This fluid must adequately wet both surfaces, and flow into the surface pores and valleys. This characteristic requires favorable values of properties such as *contact angle* and *viscosity*. By such adaptation, the *adhesive* promotes intermolecular bonding at the interface with each solid. A type of bond is formed between the solids that may be resistant to disruption by small tensile forces. This is apparent in the case of pairs of microscope slides wetted by water, which may be readily debonded, however, by shear forces.

To generate strong bonding forces, resistant to all common modes of disruption, the next requirement is that the fluid adhesive be converted to a solid. It must thus undergo a *phase change*, either by *physical* means (such as cooling from a melt or solvent evaporation) or by *chemical* setting mechanisms. The former types are widely employed in industrial and household adhesives. The latter are commonly achieved in dentistry by monomer polymerization or by acid-base setting reactions of cements. In the oral environment, there are restrictions upon permissible temperature conditions that restrict not only the possible solidification mechanisms but also the extent to which reactions such as polymerization may proceed to chemical completion. The latter is often expressed in terms of the *degree of conversion* (DC) of reactive groups in the starting monomer to the desired solid polymer state. Furthermore, the setting reaction may progress over a rather protracted period, from the *initial set* (when fluidity ceases) to a final extent of reaction.

On solidification of the adhesive, the ideal would be no change whatsoever in the adhesive-zone dimensions. However, most adhesives entail an inherent dimensional instability on setting. This is expressed, in the first instance, as a volumetric contraction or *shrinkage*. Over a longer period of time, uptake of oral fluids may lead to a gradual *expansion* that may partially or totally compensate for the initial setting shrinkage.

The setting shrinkage of solvent-based adhesives is readily understood in terms of the loss of the volume fraction of solvent. The shrinkage of polymerizing systems is conventionally understood in terms of a major (van der Waals) contribution from the exchange of intermonomer molecular spacings for the more compact covalent bonds between repeat chain units. A further (entropic) component is likely from changes in chain packing on setting. This also will be a factor explaining the setting shrinkage of glass-ionomer cements.

The overall phenomena of polymerization shrinkage are rather complex. This problem is of paramount importance in restorative dentistry. In orthodontics, the problem is less severe, because the tooth/bracket system can more readily accommodate changes in thickness across the adhesive interfacial layer. Nevertheless, any *lateral* shrinkage strain components will generate disruptive bond stresses.

In summary, adhesive solidification is essential. Nevertheless, it may be partial in extent of reaction, and brings some associated problems of shrinkage strain and stress. This leads us to consider and classify the resulting bond mechanisms holding the bracket to the tooth. For this purpose it is helpful to use the term *bonding* for the desired outcome. This can be subdivided into two components: (chemical) adhesion and (mechanical) attachment. Thus:

Bonding = Adhesion + Attachment

Under *adhesion* we would group all those contributions to bonding attributable to specific molecular interlinking *via* hydrogen bonds, London forces, and other van der Waals forces. We can include under *adhesion* the kind of molecular chain intermeshing or interpenetration of networks now known to be formed at the dentin-bond hybrid zone. Under *attachment*, we think especially of the so-called “tag” formation established with acid-etched dental enamel. This arises in situations where a highly rigid but porous substrate allows penetrating resin flow and solidification *in situ*. Mechanical interlocking is thereby attained, and this is a situation relatively insensitive to the gradual agency of adsorbed water competing for chemical bonds at the interface. Similarly, at the bracket/adhesive interface, *attachment* is the dominant contribution to bonding *via* the gross surface “undercut” detail

of the fitting surface. It follows from the preceding considerations that orthodontic adhesives should have suitable flow properties, giving wettability and penetration without undue slumping or bracket drift; this rheological characteristic is often expressed as *thixotropy*, or at least as having a yield stress before flow. The adhesives should furthermore be designed to undergo rapid initial set and to minimize setting shrinkage. Their over-

all water-absorbing tendency should be minimal.

Many other requirements that pertain in operative dentistry are of limited or no consequence in orthodontics. These include factors such as aesthetics and color stability (which may be of interest to adult orthodontic patients). We shall now examine the range of adhesive formulations that have been considered for use in this application.

The Potential Scope of Orthodontic Adhesives

Most orthodontic adhesives are variations on adhesive and direct-restorative formulations manufactured for use in restorative dentistry. The commercial reality is that competing manufacturers engage in a continual round of development and innovation. During the last quarter of the twentieth century there were two competing categories of nonmetallic direct restorative biomaterials. These may be denoted the salt-matrix and the resin-matrix types (Table 9.1) that originated, respectively, in the United Kingdom and the United States.

During the 1990s, a major development has been the *hybridization* of the technology underlying resin composites (RC) and glass-ionomer cements (GIC). That is, components from both systems have been combined in various ways with the aim of developing materials that will ideally exhibit the best characteristics of each “parent.”

Combining the characteristics of both types entails a combination of setting mechanisms and thus a mixture of network types. These various hybrids occupy positions on an almost continuous spectrum between the extremes of the pure resin composites and the pure glass-ionomer cements, both of which continue to undergo separate development (Fig. 9.3). However, in practice the spectrum is discontinuous at the point where water is either included in or excluded from the formulation. At present, there is particular interest in the possible competition between setting mechanisms and also the effect of variations in light exposure on the light-activated materials.

Table 9.1 Comparison of general characteristics of salt-matrix and resin-matrix biomaterials

Characteristic	Salt-Matrix Biomaterials	Resin-Matrix Biomaterials
Ceramic particles and size	<i>Reactive</i> : ion-leachable; release M^{n+} (and F^{-}) ions. Diameter $> 10\ \mu\text{m}$, but some $2\ \mu\text{m}$	<i>Nonreactive</i> Diameter $0.05\text{--}5\ \mu\text{m}$
Matrix precursors	<i>Aqueous</i> solutions of acidic polyelectrolytes	<i>Nonaqueous</i> dimethacrylate monomers
Setting mechanism and network type	Salt formation: ionic/covalent network	Addition polymerization: covalent network
Particle-matrix interface	Silica gel	Silane coupling agent
Initial mechanical properties	Low	High
Fluoride release	Yes	No

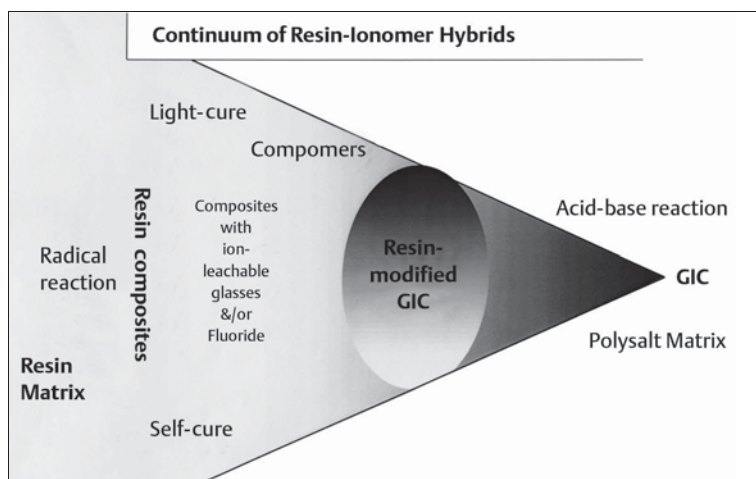
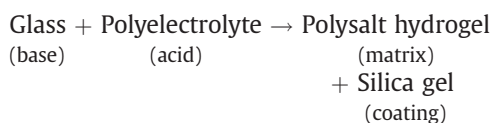


Fig. 9.3 Continuum of resin adhesives that lie between pure resin composites and pure glass-ionomer cements

Salt-Matrix (GIC) Adhesives

Glass-ionomer dental cements were invented in the late 1960s by replacing the phosphoric acid solution in the now obsolete dental silicate cement with poly(acrylic acid). This replacement required a corresponding reformulation of the glasses to make them more basic. Subsequently, a variety of other acids have been employed in glass-ionomer cements, including poly(maleic acid) and various acrylic acid-itaconic acid copolymers.

These glass polyalkenoate cements consist of an *ion-leachable* glass powder and a poly(alkenoic acid) that react together to form a cement mass by an acid-base reaction:



The development, materials science, and clinical application of GICs have been described in numerous monographs and reviews, and orthodontic uses of these cements are discussed in Chapter 11.

The advantages of glass-ionomer cements are:

- Self-adhesion to both enamel and dentin
- Fluoride release and re-release, without disintegration
- Thermal expansion coefficient similar to dentin

- No appreciable setting exotherm
- Biocompatibility in appropriate host environments
- Use in a variety of clinical applications

The typical limitations of GI cements are:

- Short working time and no “command” set (lack of control)
- Long setting time and initial sensitivity to moisture and dehydration
- Slow development of elastic modulus and strength
- Low fracture toughness (K_{IC})
- Low abrasion (wear) resistance

Stages in the Ionomer:

Acid-Base Setting Reaction of GIC

As already noted, in general this is an acid-base reaction. A number of stages may be considered, especially those of dissolution, gelation, and maturation. The kinetics of later stages are inferred, especially from long-term changes in the (flexural) modulus. The sequential stages are as follows:

1. Polyacids dissolve in water, if freeze dried.
2. Acid attack on (surface *dissolution* or *decomposition* of) the glass particles.
3. Release into the aqueous phase of Ca^{2+} ions and Al^{3+} species (probably in the form of complex oxyanions containing several Al atoms).

4. Ca^{2+} ions and PA^{n-} polyacid chains rapidly form calcium polyacrylate.
5. Slower reaction of Al^{3+} species, gradually released from the anionic complexes (formation of the initial salt-matrix: viscosity increase; *gelation*).
6. Gradual hydration, over 1–4 weeks or longer, of the released inorganic fragments (silicate and phosphate residues) to yield a secondary matrix component of increasing strength and resistance to desiccation, and with some improvement in translucency (*maturation* – final setting).

Fluoride ions and complexes are also released, but have no significance for the setting process.

Extent of GIC Reaction

The ionomer acid-base reaction is usually non-stoichiometric; that is, there is not a molecularly balanced amount of powder to react with the polyacid. Instead, there is a considerable excess of powder. However, it does not follow that all of the $-\text{COOH}$ groups of the polyacid have undergone reaction in the set material.

Resin-Ionomer Hybrids

Classification and Terminology

For some years certain manufacturers have used the term *glass-ionomer* in an extended sense to denote resin-based products that contain ion-leachable glasses but that bear only slight resemblance to traditional glass-ionomers. Strictly speaking, the term *glass ionomer* should only be used when a substantial part of the setting procedure involves an acid-base reaction. However, as already noted, traditional GICs have several disadvantages, and so more carefully designed hybrid materials have been developed.

In the wider context of materials science these may all be called *composite materials* since they consist of a *matrix phase* and a *dispersed phase*. At first, these materials were referred to as (visible) light-cured glass-ionomers (VLC-GIC), but that was not entirely appropriate terminology. Nevertheless, the new ISO (International Organization for Standardization, Geneva, Switzerland) standard is termed *Light*

Activated-Water-Based Cements (ISO 9917, Part 2). Products that fall within the scope of the standard are described as "...water-based and set by multiple reactions which include an acid-base reaction and polymerization."

Currently available resin-ionomer hybrids exhibit a wide range of composition. The principal variables that may be blended and modified are the ceramic filler particles and organic matrix-forming molecules. Regarding the ceramic powder, the common feature of virtually all these hybrids is the utilization of some form of GIC-type powder component, i.e., an ion-leachable glass. This provides a potential for acid-base reactivity and fluoride release. The glass content in formulations is typically in the range 70–75 % by weight. It follows that the *differences* between hybrid types consist primarily in the organic components, including especially the mechanisms available to activate setting. There is a spectrum of possibilities, ranging from a pure salt matrix to a pure resin matrix. These may be categorized as described in the following sections.

RM-GIC (resin-modified glass ionomers)

These set by an acid-base reaction and by free-radical addition polymerization (light and/or chemically activated). Such products should set in conditions under which no polymerization occurs. They contain components present in both glass-ionomers and resin composites.

Compomers (polyacid-modified resin composites)

These are supplied as *anhydrous single pastes* that contain some major ingredients of both resin composites and glass ionomers, *except for water*. Usually some special monomers are incorporated that include $-\text{COOH}$ groups. Exclusion of water ensures that initial setting occurs only by polymerization and is essential in preventing premature setting of the material in the container. An acid-base reaction may occur later as the material absorbs water *in vivo*, although the extent to which such a reaction can occur is probably limited. This cannot take place without appreciable water diffusion. By the time this has occurred, the self-limiting VLC-generated network will have a sufficient cross-link density to suppress extensive reaction, although the water does provide a measure of plasticization.

Ionomer-modified composites

These set only by a polymerization mechanism but contain ion-leachable glasses in an attempt to achieve fluoride release. These are further instances of so-called glass-ionomers in the extended sense, as noted above.

Resin-Matrix Biomaterials

The major current category of orthodontic adhesive systems is based upon resin composites. Dental resin composites, as already noted, are made firstly for restorative applications in large quantities, with sales in Europe alone currently totalling some US\$150 million *per annum*. The orthodontic adhesive formulations share much in common with the restorative types. They consist of two main components, an organic matrix and a powdered ceramic, such as barium aluminoborate silica glass. Particles range in size from 0.04 to 5 μm in diameter, and the volume fraction may range from 30–75%.

Organic Matrix Monomer Components

The organic matrix is formed by polymerization of an aromatic or urethane dimethacrylate. The majority of materials have been based upon the viscous aromatic dimethacrylate monomer 2,2-bis [4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane (Bis-GMA),

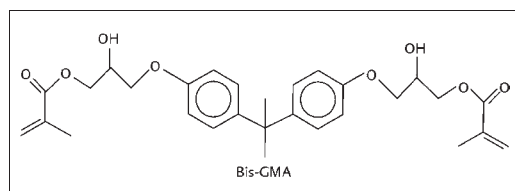


Fig. 9.4 Structure of 2,2-bis [4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-propane (Bis-GMA)

Potential Orthodontic Uses of Resin-Ionomer Hybrids

Among the preceding group of materials, it is mainly the resin-modified glass-ionomers that have attracted attention for orthodontic use. The perceived benefits are the more rapid achievement of a polymer network via free radical initiation, coupled with the release of fluoride. It is not so obvious that the compomer or similar formulations have a possible role as orthodontic adhesives.

shown in Figure 9.4. Because of its large molecular size and chemical structure, it is superior to many monomers of lower molecular mass by virtue of lower volatility, lower polymerization shrinkage, more rapid hardening, and production of a stronger and stiffer resin. To achieve a suitable viscosity in which to incorporate fillers, Bis-GMA is thinned with a variety of other monomers, of which the most commonly used have been diethylene glycol dimethacrylate (DEGMA) and triethylene glycol dimethacrylate (TEGDMA) (Fig. 9.5). A typical formulation would be 75% Bis-GMA and 25% TEGDMA, as shown in Figure 9.6.

Some materials contain alternative monomer systems in which all or part of the Bis-GMA is replaced by aliphatic or aromatic urethane dimethacrylates (UDMA) (Fig. 9.7). They have lower viscosities, hence requiring reduced proportions of TEGDMA, and have more effective light curing, lower water sorption, and greater toughness. The monomer formulation of one product is a 50/50 (by weight) mixture of urethane dimethacrylate

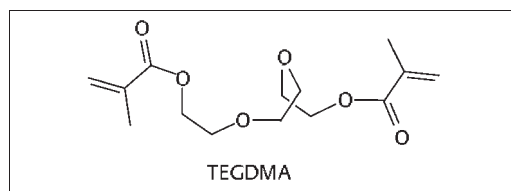


Fig. 9.5 Structure of triethylene glycol dimethacrylate (TEGDMA)

and TEGDMA. Another approach is the synthesis of Bis-EMA (Fig. 9.8), a Bis-GMA analogue that does not have the hydroxyl group in the structure, so that again a low-viscosity mono-

mer is produced that does not require large quantities of diluents. When cured, the solid may have low water sorption and less sensitivity to water than Bis-GMA.

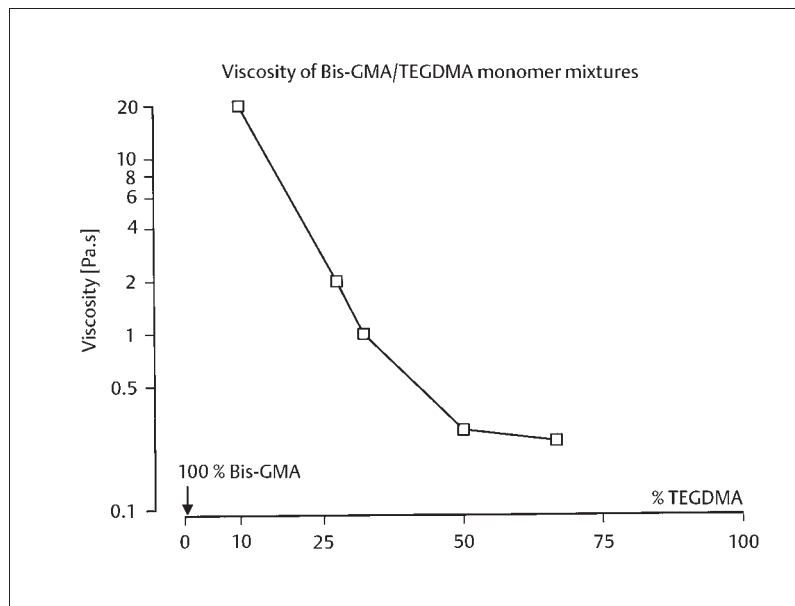


Fig. 9.6 Variation of viscosity for mixtures of Bis-GMA and TEGDMA. A typical formulation of 75 % Bis-GMA and 25 % TEGDMA is used to obtain the polymer matrix of resin composites

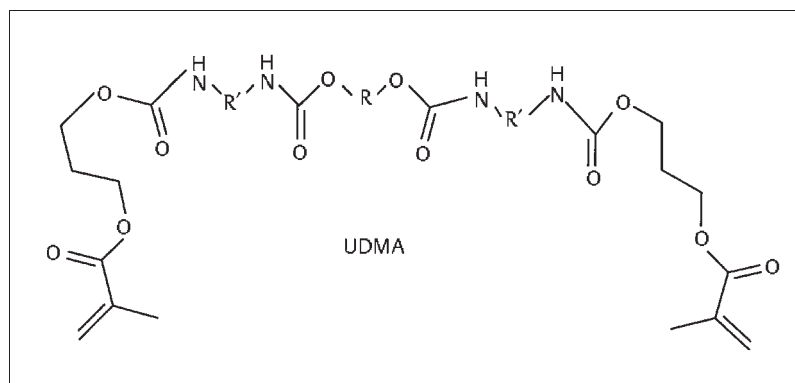


Fig. 9.7 Structure of urethane dimethacrylate (UDMA)

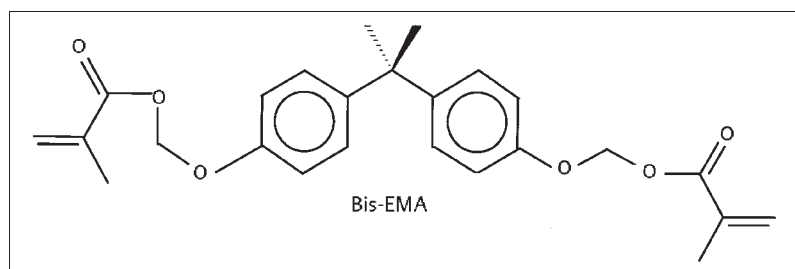


Fig. 9.8 Structure of Bis-EMA

Polymerization Activation

Two types of activation of free radicals are used in the polymerization (or *cure*) of the unsaturated methacrylate groups of these resin composites:

Self Cure (SC) These composites employ a two-paste system, one of which contains 1–2% BP (benzoyl peroxide) in the monomer portion as a free radical initiator. The activator in the other paste for these materials has usually been a tertiary amine, most commonly dihydroxyethyl-*p*-toluidine (DHEPTI), which leads to better color stability than the traditional dimethyl-*p*-toluidine (DMPTI). Yellowing of the set composite from the amine and its by-products can be minimized by the incorporation of an ultraviolet light (UV) absorber. The activator acts as an accelerator so that, on mixing, the benzoyl peroxide fragments into free radicals at room temperature, thus initiating polymerization. This type of system is most widely used in orthodontic adhesives. A particular version of this formulation that is special to orthodontics is the no-mix system, with which brackets and teeth are preloaded with complementary components of the two-part system. Contact between the bracket and tooth with the intervening adhesive permits interdiffusion of agents such as benzoyl peroxide and amine from the respective components.

Light-cure (VLC). These single-paste materials usually employ other types of free radical initiators, commonly an α -1,2-diketone such as benzil or camphoroquinone (CQ) (Fig. 9.9) and an amine reducing agent such as *N,N*-dimethyl-amino-ethyl methacrylate (DMAEMA) (Fig. 9.10) or DMPTI.

The radicalized ketone alone may initiate the photopolymerization. A reducing agent is generally added to light-cured composites for the following reason. In light-cured systems, the absorption of one quantum of radiation pro-

motes the carbonyl group to an excited singlet state. This excited state may return to the ground state by fluorescence or a radiationless transition, or it may decompose to another species. The excited singlet may also undergo intersystem crossing to a triplet state. The excited triplet then forms an exciplex with the amine reducing agent by charge transfer from the nitrogen lone pair to carbonyl, thus producing two radical ions. This reaction is significantly more efficient than the photolysis of the photo-oxidant in the absence of a reducing agent. In other words, the amine radical is responsible for initiating the polymerization and is more efficient than the radical formed from the ketone. These intensified radicals can thus significantly improve the degree of cure. The concentration of CQ photosensitizer is in the range 0.17–1.03 mass% of the resin phase and that of DMAEMA reducing agent is 0.86–1.39 mass%. The combined photosensitizer/reducing agent complex has an extended absorption band within the visible light (VL) spectrum.

Although light-curing may be problematic with metal brackets, it was first shown by Tavas and Watts that sufficient light may be transilluminated by the teeth to effect adequate photopolymerization of the material. In the case of translucent ceramic brackets, light-curing is straightforward.

An important instance of multiple setting mechanisms occurs in the case of *dual-cure* materials, which incorporate both self-cure and light-cure modes of activation. Dual-cure resin composites are increasingly used as luting agents with inlays and crowns, and these are also suitable as orthodontic adhesives. At some distance below the light-irradiated surface of a dual-cure material, the light intensity may be greatly reduced, and the extent of reaction will be strongly dependent upon the efficiency of the self-cure activated process.

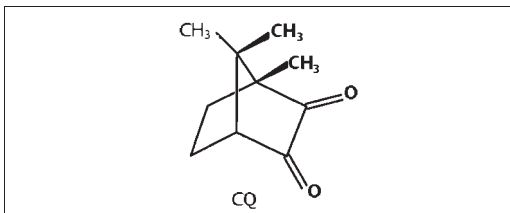


Fig. 9.9 Structure of camphoroquinone (CQ)

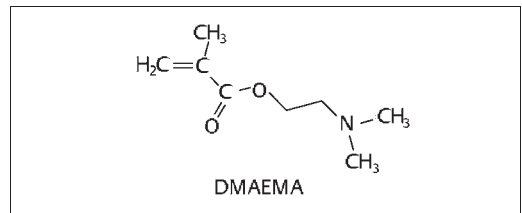


Fig. 9.10 Structure of *N,N*-dimethyl-amino-ethyl methacrylate (DMAEMA)

Reaction and Gelation

Multifunctional monomer polymerizations exhibit many *complex features*, including autoacceleration and autodeceleration, limited double-bond conversion, polymerization kinetics that are dependent upon the rate of the polymerization, and a diffusion-controlled reaction termination mechanism. Most of this polymerization behavior can be attributed to the mobility of the reacting species in the polymerizing system. For example, limited mobility of the macro-radicals leads to autoacceleration, and diffusion-limited propagation leads to maximal double-bond conversion.

Several researchers have studied the effects of increasing dimethacrylate concentration on the cure behavior of methacrylate and dimethacrylate copolymerizing systems. In general, as the concentration of dimethacrylate monomer is increased, macroscopic gelation occurs at lower conversions, severely limiting translational and segmental mobility of the polymer macro-radicals. Increasing the dimethacrylate concentration leads to higher double-bond conversion for a given polymerization time. Many such studies were conducted in the low cross-linking regime (< 5 wt% cross-linker), but they still show the dramatic effect of gelation and cross-linking density on the system mobility and the resulting polymerization behavior.

In the high cross-linking regime such as the homopolymerization of dimethacrylates, autoacceleration is apparent from the beginning of the reaction, and mobility is further restricted upon the onset of gelation. Gelation may occur even at less than 1% conversion of double bonds in many of the multifunctional monomer homopolymerizations.

The practical implications in relation to orthodontic bonding are that, once the reaction has been initiated, one should avoid disruption of the network by relative motion of the tooth and bracket.

Extent of Reaction: Degree of Conversion (DC)

The DC of resin composite materials is the extent to which carbon double bonds ($C=C$) of the monomer are converted into carbon

single bonds ($C-C$) to form polymers during the polymerization reaction. This is expected to affect the physical properties of dental composites. For chemically cured resins, the DC is influenced by the monomer composition of the resin and the concentration of polymerization catalyst within the various systems. It is evident from many studies that all of the dimethacrylate monomers undergo extensive cross-linking on polymerization, but with considerable residual unsaturation in the final product. This ranges from 25% to 45%, or equivalently the degree of conversion (DC) ranging from 55% to 75%.

The unpolymerized carbon-carbon double bonds give rise to an infrared (IR) absorption peak at 1638 cm^{-1} . This enables the determination of DC either by analysis of the filled composite, using multiple internal reflection IR, or by analysis of the unfilled resin films in transmission after extraction of the filler with a suitable organic solvent. The methods appear to provide comparable results for the same composites, although data suggest that DC is slightly reduced in composites containing large volume fractions of quartz or barium glass.

The nature of the unpolymerized resin is of considerable concern, especially in terms of deleterious effects on the mechanical properties and dimensional stability of the restoration, but less so in terms of biocompatibility (Chapter 14). The unconverted methacrylate groups must reside in the polymer network, either as residual monomer or (a majority) as pendant side chains (PSC) that extend from the main chains by virtue of having reacted at only one end of the bifunctional molecule. A further possibility is a cyclization reaction. The residual monomer molecules function as plasticizing agents that can reduce the properties of the polymer network. This occurs until such time as the monomers leach from the composite into the oral environment. Pendant side chains will act as permanent plasticizers in the composite. Hence it is desirable to increase DC in order to produce stiffer and more durable resins, although, for a given composite, shrinkage increases with DC.

Polymerization Shrinkage

Polymerization shrinkage is partially explained by a volumetric decrease arising from the conversion of van der Waals bonds into covalent bonds. This volume shrinkage for methacrylate double bonds has been shown to be approximately $22.4 \text{ cm}^3/\text{mol}$. While this explains some of the shrinkage behavior observed during polymerization, it *underestimates* the experimentally observed volume shrinkage in several cases.

If the system relaxes much more slowly than the rate of polymerization (which is often the case for photopolymerization of multifunctional monomers), an excess free volume is present in the system. This excess free volume results in greater mobility of the reacting species, which leads to a higher maximum functional group conversion.

In summary, it may be stated that there is an intrinsic shrinkage associated with resin composites and that the time dependence of this shrinkage reflects the progress of the polymerization. However, even in the "pure" unfilled resins, or in resin composites, there are subtleties to the detailed chemical behavior that are only now being explored. Consequently, when we turn to the behavior of "resin-ionomer" hybrids we may expect the detailed chemistry to be very complex.

Dispersed Phase Components

The "filler" or reinforcing ceramic phase in the early materials was a ceramic oxide, such as silica or alumina, or a glass, including some soft and hence polishable glasses. Most materials have utilized irregularly shaped particles, rather than rods or spheres, because of their better mechanical retention in the resin. Recent generations of materials have been formulated with a high proportion of hard, strong particles so as to produce composites of high strength, approaching that of tooth enamel. A high proportion of ceramic may also reduce polymerization shrinkage.

To reduce the thermal dimensional change of the resin composite to a value matching that of tooth structure, fillers have been selected from the fused-quartz form of silica or special glasses such as lithium aluminum silicate that have zero or even negative thermal expansion coef-

ficients. A further factor influencing filler selection is the need for a good refractive index match with the organic monomer to secure adequate translucence for aesthetic appearance. Radiopaque glasses containing elements such as barium, strontium, and zinc have now been substituted for all or part of the silica used in earlier products.

The incorporation of a large volume of hard filler particles has been based on the concept of attainment of high compressive strength and stiffness and on evidence that abrasion resistance improves as filler content increases and that fine fillers wear more than coarse particles. However, abrasive wear and other mechanical characteristics depend upon the particle size distribution and the manner in which they are packed together as well as the largest particle size. The original composites tended to contain particles as large as $50\text{--}100 \mu\text{m}$, but large particle sizes, especially over $20 \mu\text{m}$, cause greater difficulty in finishing and poor polishability. It has been postulated that improved wear resistance results from a filler particle separation distance of less than $0.1 \mu\text{m}$, so that the softer resin is protected from abrasion.

At the lower limit in size range are particles of pyrolytic silica, used exclusively in the so-called *microfilled* composites. Particle diameters are $0.05 \mu\text{m}$ and surface areas $\sim 50 \text{ m}^2/\text{g}$. These very fine particles act as thickening agents and create technical problems in mixing large amounts into liquid monomers. A few percent of these fillers is incorporated in composites based on fillers of larger particle size to minimize settling-out problems.

Many microfilled materials are produced by incorporation of pyrolytic silica into the monomer, which is then polymerized and ground. This ground polymer, containing the dispersed filler, is then used to make a paste with further monomer. The presence of this organic filler is also an aid in reducing polymerization contraction. By appropriate techniques, materials containing 45–50% microfine filler have been produced, and materials containing 66–70 mass % sintered filler agglomerates have been developed.

Attempts to combine the advantages of macro and microfine fillers have led to composites containing significant amounts of microfine material and a major amount of silica or

glass fillers with a particle size in the range 0.5–5 µm. A multiplicity of combinations of sizes, shapes, and particle size distributions has become available in these so-called *hybrid* materials. Improvements in the technology of grinding and dispersion of fillers have produced highly filled materials with loadings up to 87 mass% (70 volume%).

Reinforcement of the resin matrix by these inorganic fillers is achieved by strong and durable matrix-particle bonding. Coupling agents such as polymerizable silanes are used widely for this purpose.

The arrangement of particles within the set composite is a semi-random distribution, constrained by the gap-grading of particle sizes. Ideally, the distribution should be uniform between different specimens of the same material. Microfine materials commonly exhibit aggregation of pyrolytic silica particles, although this may be reduced by surfactants.

The surface profile and microstructure of composites are subject to changes arising from degradation and wear processes in ser-

vice. Polishability and surface smoothness are clinically important and are determined principally by particle size and type. In orthodontics this is of most concern in relation to clean-up procedures following debonding.

Development of Mechanical Properties

The hardness of the top surface of a VLC resin composite specimen is observed to increase with time at ambient temperatures after the cessation of light irradiation, although variation has been reported in the time-scale. The surface hardness changes should at least partially reflect changes in the bulk properties, such as elastic modulus. It is thus important to realize that the cohesive strength of the adhesive will improve subsequently to clinical irradiation with light. Similar changes in viscoelastic properties, such as static creep and creep recovery, are apparent following cure initiation as the network develops.

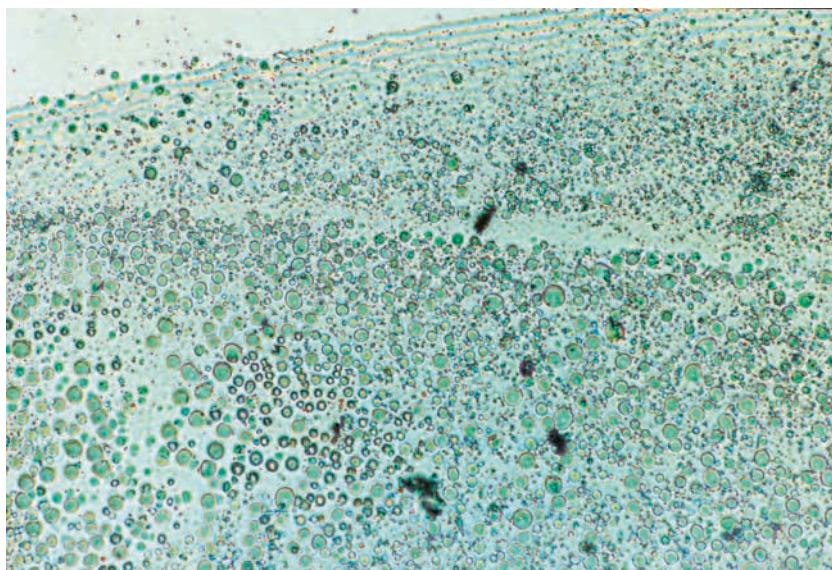
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10 Orthodontic Adhesive Resins

Theodore Eliades

George Eliades



Porosity of a two-phase, chemically cured mix of liquid orthodontic resins. Transmitted light, original magnification $\times 150$

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Introduction

Bonding of brackets to enamel has been a critical issue in orthodontics research, since the significance of achieving a stable bond between a tooth and its bracket was obvious from the outset. Biomechanical principles required a relatively inelastic interface that would transfer a load applied to the bracket, due to engagement of an activated archwire, to the tooth without exceeding its bond strength. Clinicians soon became aware of the problems related to low bond strength and the resulting necessity of repeating the bonding procedure as treatment progressed.

Early bonding systems consisted of brackets welded onto bands bonded to enamel with zinc phosphate cement. Apart from aesthetic considerations, this approach presented other serious disadvantages:

- The requirement of extensive chair time.
- The necessity of frequent screening for development of caries or decalcification of underlying tooth structure (Chapter 6).
- The pronounced effect on periodontal health due to chemical and mechanical irritation of the gingiva caused by cements and the accumulated plaque.
- The requirement of additional arch space to accommodate placement, thus affecting consideration of extraction in borderline cases and complicating the debonding owing to the interdental spacing present.

Therefore the need was clear for an alternative procedure that would provide retention of the brackets to tooth enamel without the aforementioned drawbacks of brackets welded to bands.

The introduction of an acid-etching technique in the 1950s to bond dental restorations

to tooth structure was the breakthrough point in the history of orthodontic bonding. During the mid 1950s there were some reports on direct bonding of orthodontic attachments to teeth with the use of epoxy resins, followed by the introduction of epoxy acrylates in the early 1960s and the utilization of Bis-GMA resin composites in the mid 1960s. Although conflicting evidence has been presented regarding the first use of bonding in orthodontics, the development of new adhesives and the use of known substances to provide a continuous interfacial layer with the acid-etched enamel took place in the early 1950s. The main issue at that time dealt with the extent to which orthodontic bonding temporarily altered the ion exchange between the enamel and the oral environment. This effect, along with the need for a debonding procedure that would not affect the enamel, were the main factors that influenced research trends in the field.

Consequently, the majority of the studies in this area of orthodontics have focused on evaluation of the physical and mechanical properties of the adhesive resins and sealants used for direct bracket bonding, including the early and long-term bond strength and the condition and appearance of the enamel after debonding. The main problem was the elimination of the resin layer that remained adherent to the enamel, with the resin tags penetrating into the enamel being the most important issue. These resin tags were usually subject to some discoloration due to the aging process and absorption of oral fluid components. This tooth discoloration caused some aesthetic problems and obvious patient concerns. Advances in the field have led to the development of new materials with improved properties.

Enamel-Adhesive Resin Interface

The characteristics of the tooth enamel and orthodontic brackets have been described in Chapters 6 and 7, respectively, and Chapter 5 presented an extensive description of studies that have evaluated the bonding of brackets to enamel. The purpose of this section is to reveal new evidence on the enamel morphology

and structure following etching and primer application.

It has been documented that the micro-mechanical retention of resin composites to acid-etched enamel may not be due only to formation of resin tags but also to the formation of an interfacial resin-enamel interdiffu-

sion zone within the lateral sites of the remaining enamel protuberances (Fig.10.1). This is similar to intertubular dentin hybridization in dentin adhesive systems and may explain the high bond strength values obtained from enamel, even when decreased acid-etching times are involved (Fig.10.2). Incorporation of several hydrophilic monomers into enamel bonding agents facilitates resin infiltration of

etched enamel at the prism level, reducing interfacial porosity and thus bonding defects. Based on these concepts, several new orthodontic adhesives have been introduced to improve bond strength and interfacial integrity. However, it must be emphasized that enhancement of bond strength may compromise safe debonding, as previously discussed in Chapters 5 and 7.

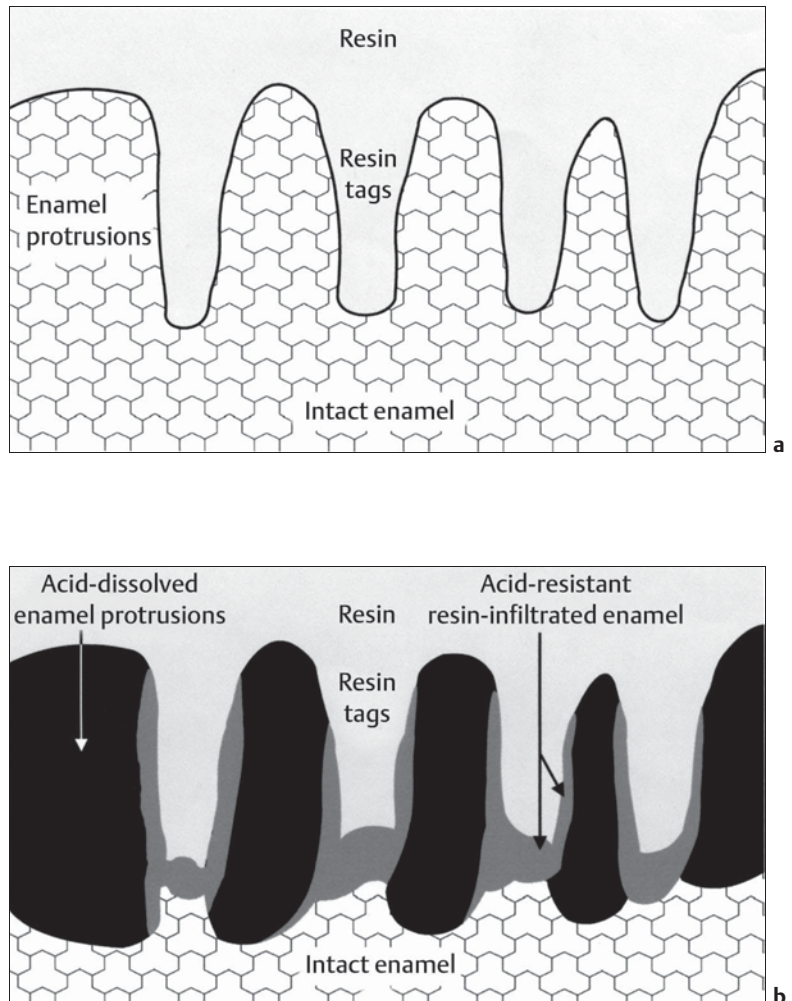


Fig. 10.1 Schematic representation of the bonding mechanism between (ortho)phosphoric acid-etched enamel and orthodontic resin adhesives. The original concept of micromechanical retention due to resin tag formation (a) has been revised. Acid treatment

of longitudinally-sectioned, etched enamel-resin interfaces removes enamel protrusions, whereas enamel regions below the resin tags are not affected owing to resin infiltration, which encapsulates enamel prisms and makes the region acid-resistant (b)

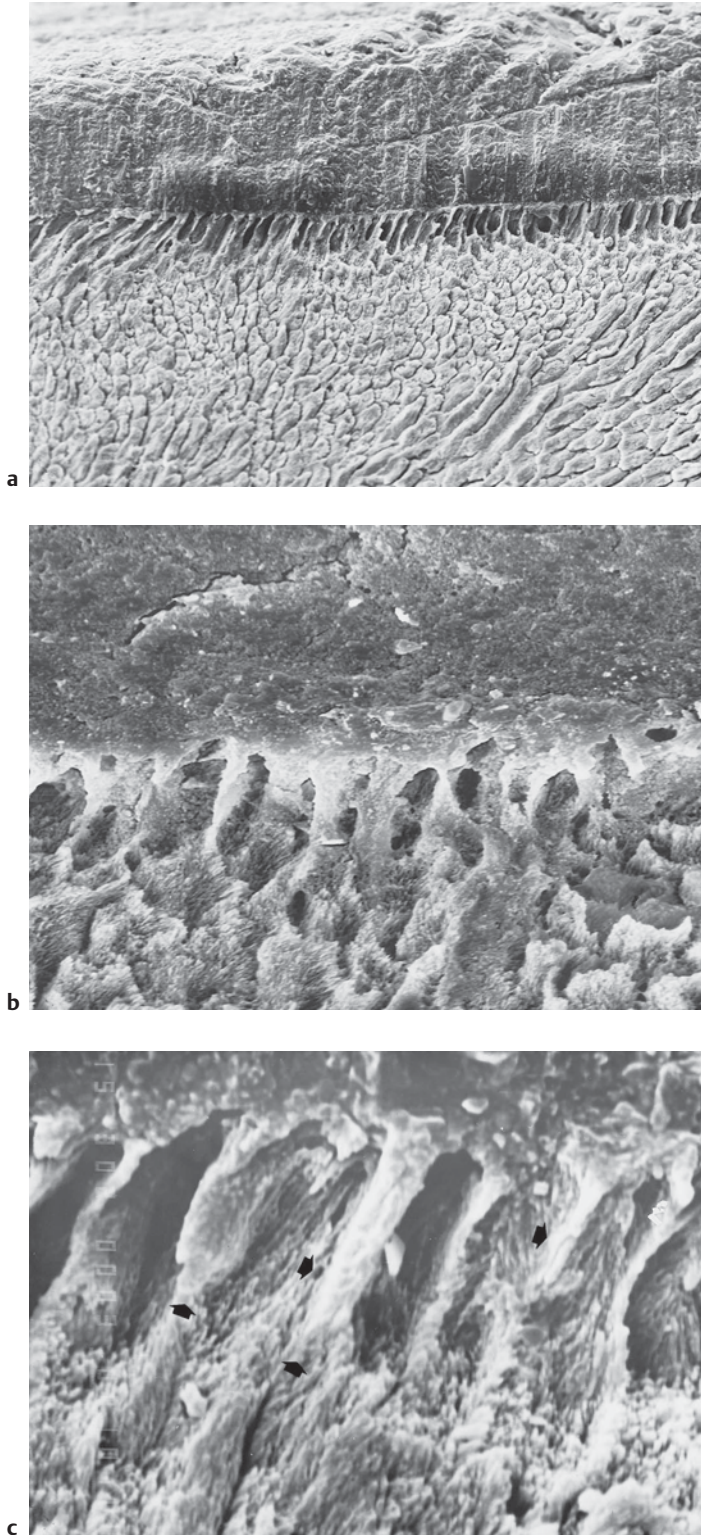


Fig. 10.2 Secondary electron images of a sectioned interface between an orthodontic adhesive and phosphoric acid-etched enamel. The interface was treated with acid for 20 seconds to dissolve enamel protrusions and to reveal the extent of resin infiltration into etched enamel of the periphery and the bottom of resin tags (arrows). (a) Original magnification $\times 400$. (b) Original magnification $\times 1000$. (c) Original magnification $\times 3000$

Bonding Agents

Unfilled resins have traditionally been utilized as bonding agents in resin composite bonding systems. The basic difference between these fluid bonding resins and the resin composites is the absence of filler particles in the former. The compositions of these systems differ from those of their composite counterparts in the increased proportion of the comonomer (e.g., TEGDMA; see Chapter 9) relative to the monomer. The use of these unfilled resins is based upon their lower viscosity and thus superior diffusion into the enamel rods, resulting in improved interfacial adaptation. However, conflicting evidence exists in the dental scientific literature regarding the necessity of their use in bonding systems. The problem arising from their use pertains to their contribution to bond strength, which has not been clearly defined.

Observations of the polymerization mechanisms and the postcuring properties for the bonding agents have been reported. Since the polymerization shrinkage is directly related to the resin volume, the unfilled resins are expected to experience higher shrinkage, thus potentially reducing the extent of enamel coverage. Also, the incorporation of a higher percentage of comonomer in these materials may result in excessive shrinkage. In addition, these unfilled resins have been found to exhibit increased water sorption, as well as an increased thickness of the oxygen-inhibited layer, because of two factors: the enormous surface-to-volume ratio involved, and the clinical procedure for placement of the resins on the enamel surface.

The first factor is exaggerated because of the period that elapses before these resins are cured. Evidence in the research literature suggests that there is no detrimental effect on bond strength for a wide range of time intervals between sealant application and bracket bonding. However, the preceding discussions in Chapters 2, 5, 7, and 9 indicate that a simple measurement of bond strength cannot adequately describe the complex phenomena occurring in polymers that are in contact with treated enamel surfaces. Moreover, there should always be concern when trying to extrapolate the results of *in vitro* tests to *in vivo* conditions.

The second factor, relating to clinical technique, arises because an increased thickness of the bonding agent on the enamel surface results in a weakened interface, owing to greater polymerization shrinkage and thermal expansion of the resin matrix. The absence of filler particles in these materials may further exaggerate these effects. Accordingly, air-thinning has been advocated clinically for decreasing the thickness of the bonding resin. However, it has been shown that with this procedure the bulk oxygen concentration in these resins may reach 60 ppm, introducing defects in the bulk material that contribute to increased water sorption and monomer leaching (in addition to the effect of oxygen on inhibiting polymerization). Since the reactivity of the oxygen-free radical complex is much higher than that of the monomer-free radical complex during the initial stage of polymerization, inhibition of polymerization occurs for the layers exposed to the air (Fig. 10.3).

Oxygen inhibition of polymerization has a detrimental effect on properties of the adhesive, causing a variation in hardness and other physical properties between the surface layers and the bulk resin. Under normal clinical conditions, the extent of inhibition depends upon both the setting time and the concentration of the inhibitor. Reactions with the affected surface may include the following:

- Formation of “oxyplex” compounds, which quench the excited states (free radicals) and subsequently suppress the polymerization process. Quenching of these excited states may lead to the production of highly reactive, single oxygen atoms.
- Scavenging of the free radical species and alteration of the polymerization mechanism.

Two different approaches have been utilized to avoid the diffusion of the oxygen into the polymerizing composite:

- Shortening of the exposure time to the air prior to complete curing. This approach includes the utilization of more powerful curing lights, incorporation of faster-reacting monomers, use of an increased photoinitiator concentration, and introduction of synergists or coinitiators to accelerate the surface cure.



Fig. 10.3 The extent of oxygen inhibition of a visible-light-cured resin (between black and white arrows). This inhibited zone is 20 μm thick. Transmitted light, original magnification $\times 100$

- Use of some means to block the resin from oxygen. Polymerization can be carried out under an inert gas, while petroleum jelly or glycerol coatings have been used to protect the resin composite from oxygen in industrial applications.

Moreover, air-thinning may induce film leveling problems and result in an uneven cured film thickness, which may lead to stress distribution problems. As a practical rule, the application of bonding agents using brushes with long and thick bristles may result in increased amounts of material being placed on the enamel surface, along with increased inclusion of air.

Classification of Orthodontic Adhesive Systems

Based upon the polymerization initiation mechanism, orthodontic adhesives may be classified according into the following groups (Table 10.1):

- Chemically activated (also termed chemically cured, autocured or self-cured): two-paste or one-paste
- Light-cured (also termed photocured)
- Dual-cured (chemically activated and light-cured)
- Thermocured

Chemically Activated Orthodontic Adhesive Systems

Chemically cured orthodontic adhesive systems have been used since the initiation of bonding in modern orthodontic history. Specific products have been utilized since the early 1970s.

However, the parameters of their *in vitro* performance have not been well defined, as noted in a critique of bond strength studies by Fox *et al.* Moreover, the *in vivo* behavior of these adhesives is poorly understood and is far from being simulated through *ex vivo* approaches. Upon reviewing 22 articles on the bond strength of a widely used chemically cured (two-phase) commercial product, Fox *et al.* found that variations in tooth type, storage conditions, method of debonding, analysis of results, and selection of other products for comparison resulted in none of the studies having the same methodology. Consequently, despite the large number of previous publications, these authors concluded that the bond strength of this commercial product had not been properly studied.

As noted in Chapter 9, the chemically activated orthodontic adhesives employ benzoyl peroxide as an initiator, which is activated by

Table 10.1 Classification of orthodontic adhesives

Adhesive	Polymerization initiation	Clinical handling	Properties	Comments
Chemically cured two-phase	Mixing of the liquid and paste components	Laborious, time-consuming	Increased exposure of components to air induces oxygen inhibition. Mixing introduces defects in the form of air entrapment and formation of voids	Appeared first in the market. Representative product: Concise (3M)
Chemically cured one-phase (no-mix)	Application of liquid component on enamel and bracket base. No mixing is involved	Efficient application, limited time requirements	Limited data on degree of cure and bond strength. Inhomogeneous polymerization pattern due to sandwich technique involved in diffusion of liquid component into paste during application. Enamel and bracket sides of adhesive are more polymerized relative to middle zones	Development of these materials succeeded the two-phase systems. May not be recommended in applications where the adhesive thickness is increased, as in bonding molar tubes. Representative products: System 1 (Ormco); Rely-a-bond (Reliance); Unite (3M)
Visible light-cured	Exposure to light-curing source	Permits increased working time for optimal bracket placement. Ideal for educational purposes. Time-consuming photocuring process. Decreased time by orthodontist and increased chair-time are involved. Photoactivation from the incisal and cervical edges is suggested	Degree of cure of stainless steel brackets bonded with light-cured adhesives is comparable to degree of cure of adhesive bonded to transparent aesthetic brackets. Bond strength has been studied extensively and supports their use	Available since the 1980s. Good alternatives to two-phase systems. Significantly more time-demanding than one-phase. Most manufacturers have marketed LC adhesives
Dual-cured	Initiation is achieved through exposure to light. Reaction proceeds following a chemically-cured pattern	Combines disadvantages of handling of both light-cured and chemically cured materials. The most time-consuming applications	Increased degree of cure and bond strength, but questionable clinical significance for their differences with light-cured materials	Introduced into the profession from prosthetic dentistry applications. Ideal candidates for bonding molar tubes

Table 10.1 continued

Adhesive	Polymerization initiation	Clinical handling	Properties	Comments
Thermocured	Initiation occurs through exposure to heat	Not intended for direct bonding	Superior properties	Polymerization initiator system restricts their use to indirect bonding. Not commonly used
Moisture-active ^a	Cyanoacrylate. No liquid component is involved. Paste formulation only. Initiation is achieved through exposure to water	One-step procedure. Enamel surface must be intentionally wetted	One study has shown acceptable bond strength	New product, possibly not marketed in the USA yet. Representative product: Smart-bond (Gestenco)
Moisture-resistant ^a	Primer compatible with the use of adhesives	Application of primer on wet enamel surface	Insufficient data available	Recently introduced. Representative product: Trans-bond MIP (3M). Light-cured Assure is claimed by the manufacturer (Reliance) to act as moisture-resistant
Adhesive-precoated bracket	Brackets covered with predetermined amount of adhesive	Direct application of primer onto the adhesive-covered base and bonding	Bond strength comparable to conventional chemically cured systems	Efficient mode of bonding. Further evidence is required for its efficacy

^a These categories do not represent distinct groups based on the polymerization initiation. However, they are listed separately owing to their having unique properties.

a tertiary aromatic amine such as dimethyl-*p*-toluidine or dihydroxyethyl-*p*-toluidine. Initiation occurs from mixing of the paste and liquid components of these systems, and free radicals are formed by a multistep process.

Two-Phase (Two-Paste) Adhesive Systems

The two-phase products were the first to be tried by orthodontists in the early days of bonding. Their application involves mixing

the paste and liquid components. The manipulative process is problematic, relatively time-consuming, and cumbersome, and these materials are gradually being eliminated from very active orthodontic practices. Mixing of the two components introduces potentially critical defects such as surface porosity and air voids in the bulk material, owing to the prolonged exposure to air and the inevitable entrapment of air bubbles. Studies have shown that photocured composites, intentionally mixed as if they were chemically cured materials, also demonstrated severely porous surfaces and air

voids in the bulk materials. The pore volume in the bulk composite was found to be of the order of 3%, while the surface porosity reached nearly 50% (Fig. 10.4). The degree of cure (DC) for these materials has been found not to exceed 55% (Fig. 10.5). The disproportionately

high amount of monomer leaching compared to the relatively high DC for a chemically cured adhesive observed by Eliades *et al* is attributed to the mixing process and to the detrimental effect of air entrapment on the carbon double-bond conversion in the vicinity of voids. The

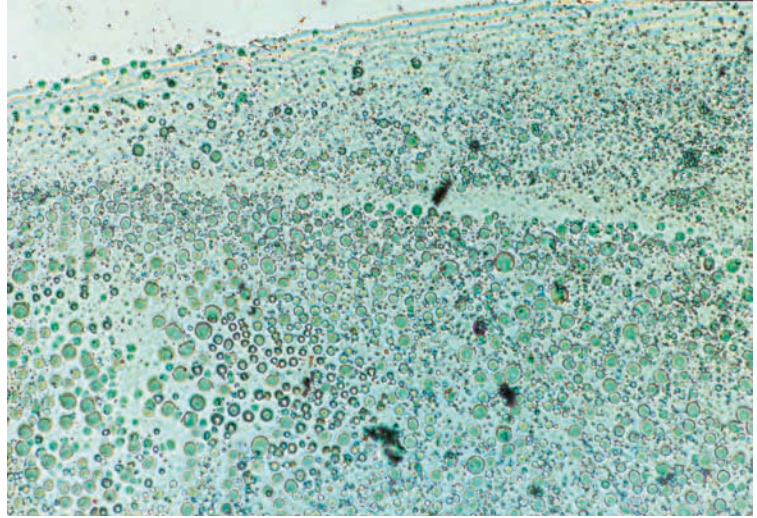


Fig. 10.4 Porosity of a two-phase, chemically cured mix of liquid orthodontic resins. Transmitted light, original magnification $\times 150$

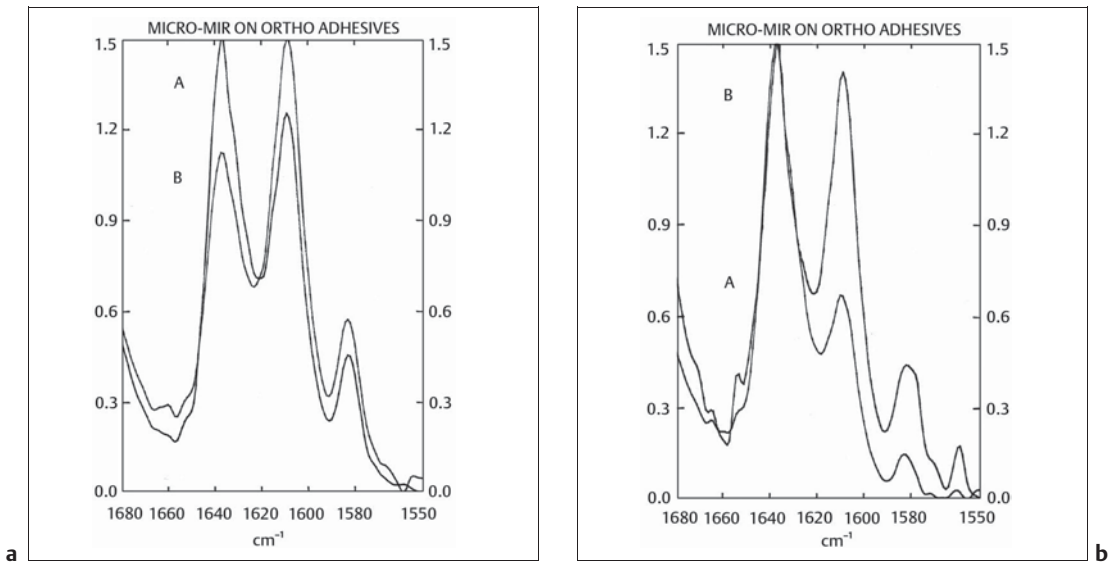


Fig. 10.5 Multiple internal reflectance Fourier transform infrared (FTIR) spectra of (a) a two-paste chemically cured adhesive (Concise) and (b) a visible light-cured adhesive (Transbond XT), before (curve A) and after setting (curve B). The visible light-cured adhesive was irradiated for 40 seconds. The reduction

in the peak absorbance area ratio of the aliphatic carbon double-bonds ($C=C$) at 1638 cm^{-1} to the aromatic carbon single-bonds ($C-C$) at 1605 cm^{-1} between A and B states, respectively, is greater in the visible light-cured adhesive, implying a better conversion

sizes of these regions of residual monomer in the cured adhesive are unknown, and their effects on biocompatibility (Chapter 14) require further study.

One-Phase Adhesive Systems

The principle of inhomogeneous polymerization was introduced in orthodontics with the development of the no-mix bonding resins, which were intended to minimize the mixing-induced defects and to reduce the steps required for placement of the material. In these systems, a catalyst gradient is established from the primed enamel surface toward the brackets by means of a diffusion process. Under these conditions, the resin strength is presumed to be decreased by the establishment of a disturbed cross-linked network, which nonetheless may facilitate bonding.

However, recent evidence suggests that the DC for these adhesives is comparable to that of the two-paste systems for surfaces in contact with the enamel. This might be attributed to the surface-to-volume ratio of the adhesive layer, which can depend upon several factors. A study found that the thickness of adhesive layers prepared under simulated clinical conditions ranged from 120 to 230 μm , depending upon the morphology and design of the bracket base. The mean layer thickness is especially increased when complex bases possessing grooves and crystal-like projections (Chapter 7) are pressed into the adhesive, presumably owing to the retention of material in the base. However, this effect depends strongly on the topography of the base and the viscosity of the adhesive. In general, sharp crystals protruding from the base should act to increase the local stress on the adhesive. In contrast, smooth bases would be expected to transfer the applied force more uniformly to the adhesive layer. It is further assumed that, when applying the bonding agent to the tooth surface and bracket base, the diffusion process required for polymerization is intensified by pressing the bracket to the enamel.

Light-Cured Bonding Systems

Background and Basic Concepts

For a monomer system in which light-curing is used to initiate polymerization, the extent of polymerization depends upon several factors: the exposure time, the photoinitiator concentration, the light intensity emitted by the curing unit at the peak absorbance wavelength of the photoinitiator, and the filler volume fraction.

The spectral distribution of the light source significantly affects the polymerization of the material. The light intensity at the peak absorbance wavelength (λ) of the photoinitiator, as well as the length of the light exposure, have great impact on the degree of conversion of the resin (Fig. 10.5). Light scattering at the surface of the filled composite can reduce the intensity of the incident light reaching the bulk material, resulting in significantly decreased conversion in thick specimens. The filler size is a critical factor for the degree of scattering, and the optimal particle size is $\sqrt{\lambda}/2$.

The frequency of light emission from the curing unit is also important. Under steady-state polymerization conditions, the free radical concentration (v_p) is proportional to the square root of the light intensity (I) over the range for the peak absorbance wavelength ($v_p \propto I^{1/2}$), when the light intensity is constant or when the flashes from an unstable light source are rapid. At lower emission frequencies from the light source, the free radical concentration decreases by a factor of $\sqrt{2}$.

Under clinical conditions, increased irradiation time and light intensity lead to higher strength for the photocured composite, since a structure with a higher density of cross-links is formed. With light-curing from the edges of the bracket, the directions of the free-radical gradient and the polymerization shrinkage are modified from those of the chemically cured no-mix materials. In addition, the rapid setting reaction for the relatively thin layers of photocured composites greatly reduces the time available for atmospheric oxygen to diffuse into the bulk resin and deactivate the free radicals produced by the photoinitiator. As a result, superior mechanical properties (because of significantly less oxygen inhibition) and better peripheral bracket sealing are obtained with light-cured composites compared to chemically cured systems.

Applied Research on Light-Cured Adhesives

A number of studies published during the 1990s have investigated the bond strength and DC of light-cured adhesives bonded to transparent ceramic brackets and metallic brackets. The majority of these studies concluded that the bond strength provided by the light-cured material was not different from that for the chemically cured adhesive.

In a study by Eliades *et al* the DC value for a light-cured adhesive bonded to a metallic bracket and irradiated from the incisal and cervical edges was comparable to DC values for a chemically cured adhesive and its light-cured counterpart bonded to transparent ceramic brackets. These observations may be explained by considering that the adhesive was exposed to light originating from two sources: the light-curing unit and secondary illumination due to reflectance from the artificial background surface used in the study.

It is also important to note that, in this study, light activation involving only one bracket at a time was performed, in contrast to earlier instructions from the manufacturer advocating simultaneous irradiation of two adjacent brackets. Since the light intensity varies as the inverse square of distance, it is critical to maintain close contact between each bracket and the light source.

A report based on microhardness measurements has claimed that secondary illumination is of low intensity and insufficient to induce adequate conversion. However, the mode of light application in that study was exclusively from the lingual surface of the tooth and therefore not comparable with the average clinical procedure which involves photocuring of the adhesive from the incisal and cervical edges of the bracket. Use of a “sandwich” pattern of light activation and illumination from the enamel in clinical practice may reduce the light intensity required to initiate polymerization.

Eliades *et al* have also investigated the variability of the DC for light-cured adhesives as a function of the light transmittance of ceramic brackets. It was found that the relative dimensions of the light-curing unit tip and the bracket base accounted for some of the differences noted. Since the dimensions of the light source tip are much greater than those of the bracket

surface, it is likely that the path of photoactivation is not important when the light intensity is sufficient. The results of this study have been confirmed by an article demonstrating no difference among several light tip configurations with respect to bond strength results. This observation supports the proposed concept of a critical light transmittance and a “threshold” light intensity for polymerization of adhesives to be initiated with ceramic brackets. Evidence suggests that exposure to very high curing light intensity does not result in correspondingly high DC.

Research has shown that the DC of the light-cured Transbond XL (3M Unitek) adhesive bonded to polycrystalline alumina brackets was not significantly different from that of the chemically cured Concise (3M Unitek) adhesive bonded to the same brackets. This result is attributed to the thin film nature of the adhesive layer, which has a very high surface-to-volume ratio. The dominance of surface properties over bulk properties is considered to favor the use of light-cured adhesive resins, because these systems are expected to possess superior surface curing characteristics.

Dual-Cured Systems

The dual-curing approach combines the advantages of rapid initiation for photopolymerizing resins and high conversion rates for chemically cured resins in the bulk material. In these systems, activation of polymerization is induced through surface exposure of the material to a source of visible light, and polymerization in the bulk material occurs by a chemical curing process. Therefore, both improved surface and bulk material properties would be expected. Limited documented experimental bond strength data available in the literature support the clinical efficiency of these systems. In a study, the dual-cured adhesive was found to provide significantly higher bond strength compared to chemically cured and light-cured materials 24 hours following activation. The DC value obtained for this dual-cure initiation mode was the highest among the adhesive types used. However, the clinical application process for this type of adhesive is prolonged because both mixing and photocuring are required. Moreover, mixing may introduce bulk

defects, as previously discussed for chemically cured adhesives, increasing the porosity of the material.

Thermocured or Heat-Activated Systems

Systems of this type have been introduced for indirect orthodontic bonding and restorations. It is claimed that these adhesives present substantially increased polymerization rates and, accordingly, superior properties. However, their use is currently limited because of the increased temperature required to initiate polymerization and the necessity for adapting an indirect bonding setup.

Moisture-Active Adhesives

There has been an increasing interest by the manufacturers to introduce adhesives that can perform in the presence of moisture (Fig. 10.6). Despite the moisture-control steps and measures available, the orthodontist often faces the problem of bonding in an environment with increased risk of contamination from saliva. This may be a particular concern

during bonding of partially erupted premolars, where many bracket failures occur. Problems arise because of the proximity of the adhesive to the cervical portion of the crown and the presence of crevicular fluid, as well as the contour of the crown. It is important to note in this context that the term “wet” refers to the presence of water, while saliva or crevicular fluid are considered to be contaminants.

While some manufacturers claim acceptable performance for their products in a wet environment, others have introduced moisture-active adhesives. The former type of product, which may be termed a *moisture-resistant* adhesive (Table 10.1), is available in a primer formulation that replaces the conventional bonding agents applied to the enamel surface and is based on the hydrophilic attraction of its constituents. The main reactive component of this product is a methacrylate-functionalized polyalkenoic acid copolymer originally used in the dentin bonding system marketed by the same manufacturer. Excess interfacial water ionizes carboxylic groups, forming hydrogen-bonded dimers (Fig. 10.7). Moreover, a reversible breaking and reforming of calcium-polyalkenoic acid complexes with enamel is established, providing some stress relaxation capacity. In this manner, a dynamic equilibrium occurs at the interface, incorporating water in the bonding mechanism, thus minimizing the detrimental plasticizing effect of water that occurs with moisture contamination of conventional bonding agents.

In contrast, *moisture-active adhesives* (Table 10.1) *require* rather than tolerate the presence of moisture for proper polymerization. These materials are available as pastes and possess a completely different composition and poly-



a



b

Fig. 10.6 Moisture-active primer (a) and adhesive paste (b)

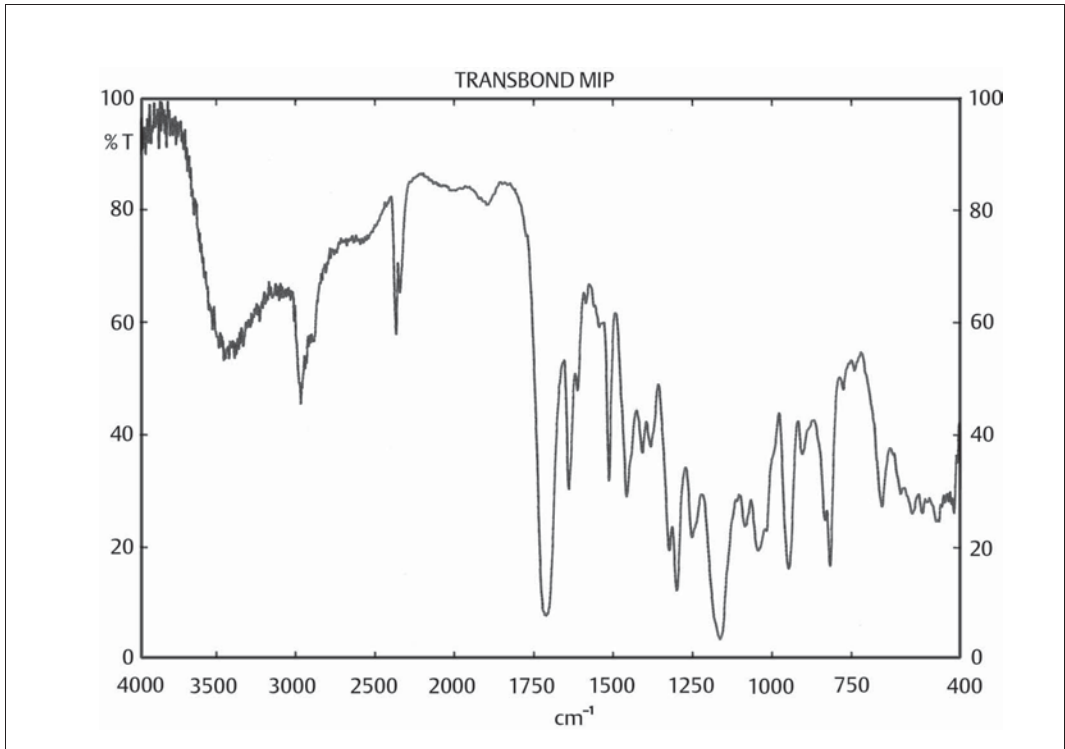


Fig. 10.7 FTIR spectrum of a moisture-insensitive orthodontic bonding agent (Transbond MIP). The primer is based on a methacrylate-functionalized polycarboxylic component that gives a characteristic broad band over the 2750–2500 cm^{-1} region, due to the formation of hydrogen-bonded carboxylic dimers

merization mode, requiring no bonding agent. However, the surface must be intentionally wetted prior to application. A recent product based on a cyanoacrylate formulation (Smartbond, Gestenco International AB, Sweden) has demonstrated superior properties, excellent *in vitro* performance and easy clinical application without the need for etching and liquid resin coating. The setting reaction of this product involves two steps. In the first step isocyanate groups react with water, forming an unstable carbamic acid component, which rapidly decomposes to carbon dioxide and the corresponding amine. In the second step the amine reacts with residual isocyanate groups, cross-linking the adhesive through substituted urea groups (Fig. 10.8). However, in the presence of excess water only the first step of the reaction takes place, resulting in the formation of deleteriously brittle polymer films. An additional problem with these systems may be the release of carbon dioxide during the prolonged setting

reaction. The carbon dioxide is capable of only limited diffusion through the adhesive film as polymerization proceeds and may become entrapped, forming gaps or voids with detrimental effects on the interfacial strength. Further research is necessary to elucidate these phenomena in greater detail.

As always, extrapolation of clinical performance from *in vitro* tests must be done with considerable caution. This is because the wet environment in the oral cavity is mostly due to salivary flow rather than to the presence of water; the orthodontist can adequately protect the bonding surface from water contamination. The manufacturer emphasizes that contamination with saliva must be avoided, because this will disturb the setting process and adversely affect the structure and performance of the material. Because of their past success in industrial applications, these moisture-active adhesives were transferred to the dental profession as ideal candidates for the wet environment.

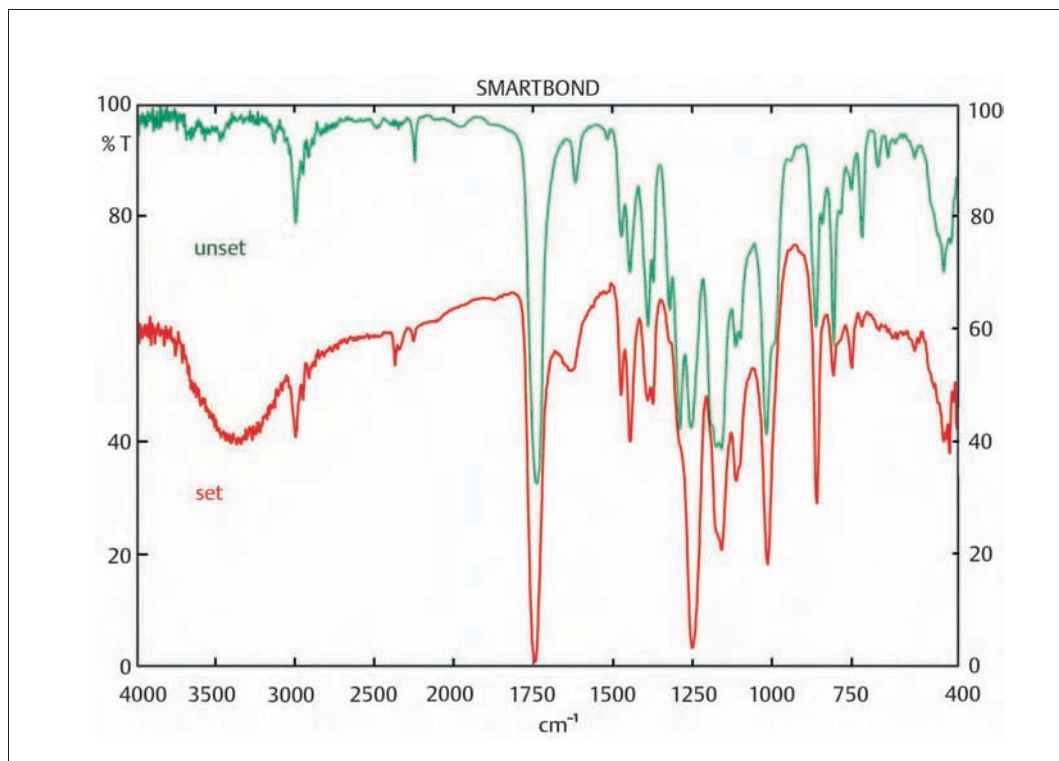


Fig. 10.8 FTIR spectra of a moisture-active orthodontic adhesive (Smartbond) before and after setting. The intensity of the original isocyanate group (-NCO at 2239 cm^{-1}) is reduced in the set film owing to the formation on the polyurethane amide backbone. The set film contains hydrogen-bonded water (-OH at 3400 cm^{-1}) and an increased content of CO_2 (2364 cm^{-1})

The presence of saliva, however, may adversely affect their long-term clinical performance. This may be an important area for future investigations and the development of improved adhesives.

Precoated Brackets

Almost a decade ago the concept of adhesive-precoated (APC) brackets was introduced, and a product was marketed. Manufacture of the APC bracket was based on objectives of increased bonding efficiency and standardization of the bonding procedure, which presumably would be beneficial for the clinician (Table 10.1). Research showed that the APC system had decreased bond strength compared to the conventional manual application of an adhesive that had been refrigerated for one week. However, the small difference found

between the APC system and the conventional approach of adhesive application to the brackets may be clinically insignificant, particularly because of the absence of standards. Consequently, application of the APC approach to clinical conditions may have merit and should be investigated further.

Degradation of Polymeric Systems

General Principles and Background

Degradation of high polymers can be characterized into two broad areas:

- *Random*, where chain rupture is induced by one or more factors, such as exposure to ozone, oxygen, ultraviolet radiation, and foreign agents. This type of degradation occurs at random sites in the polymer structure, resulting in the release of large structural fragments.
- *Chain depolymerization*, where release of monomer occurs in a more organized manner (depropagation).

Depropagation is virtually the reverse of polymerization, where bond breakage is initiated at a chain defect site and a hydrogen atom is released from the polymer structure. The polymer chain then splits, and both a free radical and an inactive species are created.

Critical factors in this type of degradation are the reactivity of free radicals and availability of hydrogen atoms. Evidence of the role of the hydrogen has been presented on the basis of preferential attack at branching sites of the poly(methyl methacrylate) (PMMA) structure and inhibition of chain depolymerization induced by hydrogen-blocking agents.

Research has shown that water sorption and the resultant composite resin solubility initiate microcracks or enlarged diffusion channels due to swelling. Localized bacteria and enzymes may then penetrate the surface of the resin and accelerate the degradation process. Since there is a definite link between water sorption, solubility, and polymerization, increased monomer concentration and carbon double-bond unsaturation might predispose the material to potent degradation reactions. Evidence of the detrimental effects of enzymes and enzyme metabolism by-products on dental resin surfaces has been presented in the literature. Munksgaard and Freud demonstrated the occurrence of enzyme-induced degradation of dimethacrylate polymers and the hydrolytic nature of the process. Their work was preceded by experiments in several polymer systems that consistently showed enzymatic activity-induced degradation of the materials. Initially,

the applicability of these laboratory results to the clinical situation was questioned. Investigators claimed that, under clinical conditions, the composite resin is covered by a proteinaceous film (pellicle) that masks the surface layer, presumably decreasing its reactivity with the environment and any subsequent attraction and adsorption of molecular complexes. Such adsorbed substances might affect the enzymatic activity of adjoining resin molecules in an unpredictable manner.

However, Matasa has demonstrated that aerobic and anaerobic microbial activity may weaken the resin, leading to compromised bond strength. Evidence indicating microbial attack of adhesives attached to brackets being debonded has been presented. These effects were attributed to the ability of some microbes to metabolize adhesive constituents. A suggestion was made to incorporate substances in the adhesive with bactericidal activity, similar to the approach of including gentamycin in bone cements (PMMA-based) intended for use in total hip replacement arthroplasties. However, no documented evidence regarding the feasibility of introducing such a product is currently available.

Leaching of Orthodontic Adhesives

This section considers from a materials perspective the elution of substances from cured adhesives. Possible biocompatibility problems resulting from such leaching processes are considered in Chapters 14 and 15.

Published studies are contradictory with respect to the qualitative and quantitative parameters of elution, because varying methodologies have been employed. Water immersion has been reported to cause release of 50% of the leachable species from dental resins during the first three hours, while ethanol-water immersion accelerated the release rate to 75% of the molecules eventually eluted over the same period of time. Ferracane and Gordon were unable to detect further elution from composite resins after 24 hours of immersion, regardless of the solvents used. In contrast, other investigators found prolonged elution from composite resins and orthodontic adhe-

sives, which continued for 115 days and two years, respectively.

Differences in the solvents used for leaching experiments have been found to affect both the quantity and composition of eluted substances. Ethanol-water baths tend to accelerate the degradation of composite resins when compared to water immersion, and also promote elution of leachable species in different proportions.

As discussed in Chapters 14 and 15, the quantity and composition of the eluted substances are key factors for the toxic potential of a resin adhesive. In general, the maximum accepted weight loss of a restorative material has been stipulated at $5 \mu\text{g}/\text{mm}^3$ according to ISO Standard 4048 (E). However, amounts of up to $9 \mu\text{g}/\text{mm}^3$ of leachable species have been reported. Filler components (mainly silicon) have been estimated to account for approximately $180 \mu\text{mol}/\text{g}$ weight loss. The maximum accepted values of weight loss based upon laboratory assays are typically established for restorative materials to minimize their adverse effects *in vivo*.

Eluted substances include fillers, enzymatic hydrolysis-induced methacrylic acid, benzoic acid resulting from degradation of the benzoyl peroxide initiator, and other noncharacterized materials probably originating from the polymerization accelerators and catalysts. A serious concern arises from the formation of formaldehyde ($\text{H}_2\text{C}=\text{O}$) as an oxidation reaction product of oxygen with the carbon-carbon double bonds. Oxygen is capable of detaching the pendant group from the polymer network, leading to structural degradation and the formation of compounds of suspected or known biocompatibility problems, such as formaldehyde, in amounts of the order of $0.1 - 0.5 \mu\text{L}/\text{cm}^3$.

Both residual monomer and the presence of unsaturated carbon double bonds have been blamed for the prolonged and increased elution of toxic reactants from dental resins. The combination of different monomers seems to be more detrimental than a single monomer species.

The effect of the monomer molecular weight on the toxic potential of the resin is a matter of disagreement. Monomers with decreased molecular weight are expected to have a higher degree of conversion and consequently less potential to initiate toxic reactions. In agreement with this concept, monomers of increased mo-

lecular weight have been found to show increased toxicity. Fujisawa and Mashuhara noted the potential of hemolytic activity for Bis-GMA. Caughman *et al* and Rathbun *et al* showed that the monomer does not apparently contribute to the toxicity of dental composites by providing evidence for lack of correlation with cytotoxicity data; the toxic effect of resin matrix plasticizers was emphasized.

Eliades *et al* have investigated the elution of Bis-GMA and TEGDMA residual monomer from orthodontic adhesives bonded to ceramic and metallic brackets. An ethanol-water (75% ethanol) solution was chosen as an immersion medium because previous research indicated the occurrence of prolonged monomer release over a two-year period. Immersion of resins in the 3:1 ethanol-water solution was found to increase the rate of monomer release and the degradation reactions by introducing accelerated aging.

The highest values for the unsaturated TEGDMA concentrations in the light-cured resin were obtained with use of a composite ceramic bracket with a flexible plastic base, followed by use of a metallic bracket. No other ceramic bracket yielded comparably high values for TEGDMA in this adhesive. Moreover, use of the stainless steel bracket resulted in substantially increased TEGDMA concentration in the adhesive layer compared to the other alumina brackets. This can be attributed to the decreased light intensity (direct activation) reaching the adhesive layer with the metallic bracket and the associated reduced free radical formation. A considerable decrease in the TEGDMA concentration also occurred when indirect activation was used to bond the metallic bracket to the light-cured adhesive. This result also suggests that insufficient available light intensity was probably the reason for the elevated monomer unsaturation.

The residual Bis-GMA concentrations found in this study were generally similar for both two modes of activation. An interesting observation is that, while the highest Bis-GMA concentration was also found for the metallic and ceramic-plastic base brackets, the ranking was reversed from that for the TEGDMA results.

The chemically cured adhesive used in the study exhibited increased monomer concentration values relative to the light-cured adhesive. However, disproportionate differences

between DC and monomer leaching were noted with the two adhesives. Although values of DC measured for these two adhesives were only slightly different, the residual monomer concentrations for both TEGDMA and Bis-GMA differed considerably. This observation may be explained by the increased mixing time and the prolonged polymerization process for the chemically cured adhesive.

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Aphrodite Kakaboura

George Vougiouklakis



Photograph of the *in vitro* failure site for a bracket bonded with glass-ionomer cement, showing cohesive fracture through the adhesive where a layer of the material remains on the enamel

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Introduction

Dental cements are used for retention (luting) of preformed restorations and orthodontic bands, thermal and chemical insulators under restorative materials to provide pulpal protection, temporary or permanent restorations, and root canal sealers. This multiplicity of applications necessitates a wide variety of characteristics and a complex profile of properties. The cements may be classified by composition into four categories: (a) phosphate, which includes the zinc phosphate and silicophosphate cements; (b) phenolate, which includes the zinc oxide-eugenol and calcium hydroxide cements; (c) polycarboxylate, which includes the zinc

polycarboxylate and glass-ionomer cements; and (d) resin cements. Some aspects of the glass-ionomer and resin cements have been discussed in Chapters 9 and 10.

The orthodontic application of cements is limited to luting of appliances. For acceptable performance, a luting material should possess a variety of properties: adequate working and setting times; high tensile, compressive and shear strengths; resistance to dissolution; clinically acceptable bond strength and low Adhesive Remnant Index (ARI) score (Chapter 5) following debonding; and anticariogenic potential.

Zinc Phosphate Cements

Zinc phosphate cements are widely used for cementation of orthodontic bands. These cements are generally available as hand-mixed powder-liquid systems, although some encapsulated products are marketed.

Composition

The principal active constituent of the cement powder is zinc oxide (Fig. 11.1). A small quantity of magnesium oxide may also be identified in some currently available products. Various cement powder formulations may include small amounts of additives such as silica or alumina, while other brands contain approximately 10% fluoride in the form of stannous fluoride. The latter products are generally recommended for cementation of orthodontic bands because of their anticariogenic effect from the release of fluoride (Chapter 6). The addition of magnesium oxide to these cements results in improvement of mechanical properties as well as color stability. The additions of silica and alumina also increase the mechanical properties, while providing a variety of shades for these products.

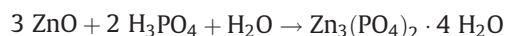
The components of the powder are sintered at 1000°–1350°C for several hours and then ground into fine particles. This procedure reduces the reactivity of the powder and moderates the setting reaction, yielding adequate

working and setting times for the cement. The magnesium oxide facilitates sintering of the zinc oxide powder; smaller powder particles produce a more rapidly setting cement.

The liquid is essentially an aqueous solution of phosphoric acid in concentrations varying from 45% to 64%, buffered by small quantities (2–3%) of aluminum phosphate and, in some products, zinc phosphate (1–9%). The metallic salts form an amorphous phosphate, resulting in stabilization of the pH of the liquid and reduction of the reaction rate; this allows the mixing of a higher quantity of powder with the liquid. The water content influences the setting rate of the cement, since it regulates the ionization of the liquid.

Setting Reaction and Structure

When the cement powder and the aqueous liquid are brought together, the acid attacks and dissolves the outer layer of the zinc oxide particles, releasing zinc ions into the liquid. At this stage, a rapid, vigorous exothermic reaction occurs, leading to the formation of hydrated zinc phosphate, as follows:



The course of the reaction is shown by the pH changes of the cement. Two minutes after mixing the pH is 1.6; after one hour the pH in-

Fig. 11.1 Secondary electron image of the powder particles of a zinc phosphate cement. Original magnification $\times 1000$

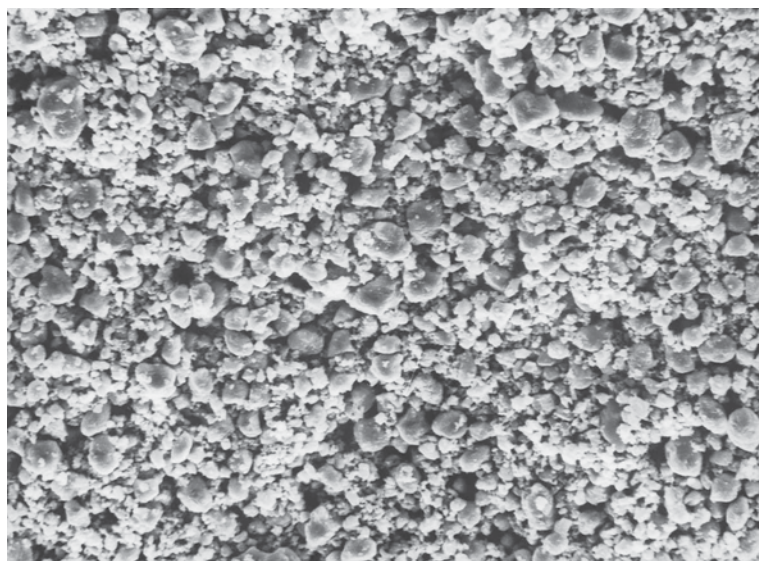
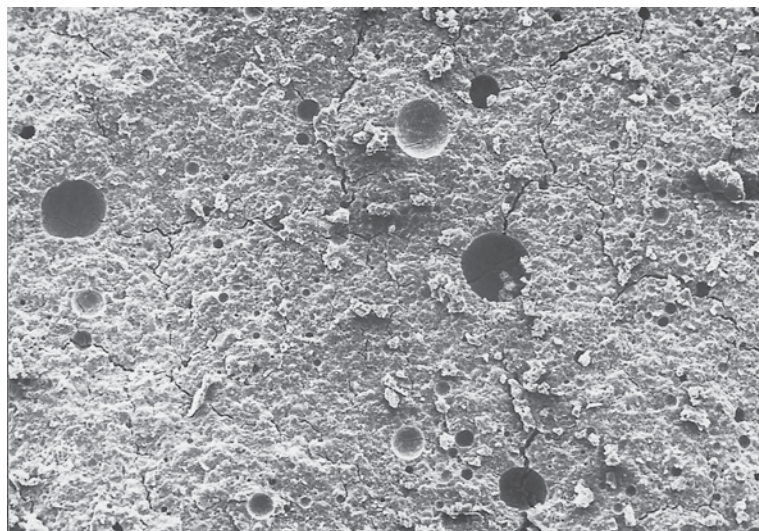


Fig. 11.2 Secondary electron image of porosity in a set (48 hour) zinc phosphate cement. Original magnification $\times 200$



creases to about 4.0, and after 24 hours it ranges between 6.0 and 7.0. Although the role of aluminum in the setting reaction has not been clearly defined, it has been suggested that aluminum may produce complexes with phosphoric acid, forming a glassy zinc aluminophosphate gel on the surface of the unreacted zinc oxide particles. The incorporation of buffers into the liquid, as well as the method employed by the manufacturer for production of the zinc

oxide powder, may moderate the reaction rate. The structure of the set cement consists of residual zinc oxide particles (termed "core" in some dental materials textbooks) bound together with a matrix (reaction products) of an amorphous, relatively insoluble gel of zinc, magnesium, and aluminum phosphates. The fully set cement exhibits porosity as a result of entrapment of air during mixing of the powder and liquid (Fig. 11.2).

Working and Setting Times; Manipulative Variables; Film Thickness

The powder-to-liquid ratio and the consistency of the mixed paste for the zinc phosphate cement largely depend upon the particular dental procedure and the properties desired for the cement. The powder-to-liquid ratio for the cement strongly affects the working and setting times. A thin consistency (low viscosity) is essential when the cement is used as a luting agent, to ensure adequate flow during cementation of orthodontic bands. The relatively fluid mixture is obtained by decreasing the powder-to-liquid ratio.

Several manipulative variables may affect the consistency, the working time and the setting behavior of the cement. An extended working time and a "sharp" set (very rapid increase in viscosity) are of fundamental importance in banding. A reasonable working time for zinc phosphate cements ranges between 3 and 6 minutes, and the setting time should be between 5 and 9 minutes, as specified in ANSI/ADA specification no. 96 (ISO 9917) for dental water-based cements. For optimum results, the powder should be incorporated into the liquid in small portions and at a relatively slow rate to achieve the desired consistency. With this method the exothermic setting reaction is retarded, with a reduction in heat generation. The viscosity of the mixture remains low, and the working time is optimized. In contrast, rapid mixing of the cement powder and liquid causes substantial heat evolution, with considerable decreases in the working and setting time.

Mixing of the powder and liquid over a large area of the glass slab also results in a lower temperature increase from the setting reaction and provides extended time for manipulation. The use of a cooled and dried mixing slab retards the reaction rate and prolongs the working time without influencing the setting time. In general, an extended working time allows the incorporation of greater amounts of powder into the liquid to produce a stronger and less soluble cement. However, care must be taken not to cool the slab below the dew point, since condensation from the air can cause contamination by water. Excess water may affect both the setting characteristics and the physical and mechanical properties of the cement. The

addition of small quantities of powder to the liquid one minute prior to initiating mixing can prolong the setting process.

In hand-mixed products where the cement liquid is kept in a bottle, the cap should be removed only long enough to dispense the liquid portion for the mixture. Otherwise, the liquid may lose or gain water from the air, altering the setting behavior and the properties of the cement. The liquid should not be dispensed and allowed to remain on the slab for a substantial time prior to mixing, as some of the water contained in the liquid will evaporate. Prolonged spatulation should be avoided since this procedure may disturb the formation of the matrix of setting reaction products.

Since adhesion has not been documented to develop between zinc phosphate cements and orthodontic bands, retention of the bands is attained by mechanical interlocking. Thus, the film thickness of the cement placed between the band and the tooth is of paramount importance. Thin films result in substantially better cementation, as internal flaws within the cement are minimized, and there is better adaptation at the cement-tooth interface. In general, a film thickness of approximately 20 μm may be achieved with zinc phosphate cements, which is considered satisfactory since ANSI/ADA specification no. 96 suggests that an acceptable film thickness is of the order of 25 μm . The film thickness is a function of powder particle size, powder/liquid ratio, and viscosity of the cement mixture. Band placement should take place when the cement mixture flows, as the increased viscosity occurring with time may result in greater film thickness, leading to poorly retained and inadequately adapted bands.

Properties

Strength

Although an initial rapid rise in cement strength occurs in 4 to 7 minutes after mixing, reaching 50% of the final strength, the strength continues to increase at a slower rate for approximately 24 hours. Zinc phosphate cements, when properly manipulated in the luting consistency, exhibit compressive strengths ranging between 80 and 140 MPa.

The greater range of strength values reported in the literature may arise from the composi-

tional variation for the different products. According to requirements in ANSI/ADA specification no. 96, the compressive strength for zinc phosphate cement should exceed 70 MPa. A linear relationship has been shown between the compressive strength and the powder/liquid ratio.

The (uniaxial) tensile strength of zinc phosphate cements is much lower than the compressive strength; their diametral tensile strength is typically less than about 5 MPa. The differences in tensile and compressive strength reflect the completely brittle nature of these cements. Values for modulus of elasticity in compression range for luting cements from about 9 to 13 GPa, and these cements can be considered as relatively stiff materials. The lower compressive and tensile strengths of luting cements, compared to the corresponding values for cements intended to be placed beneath restorations to serve as thermal and chemical barriers, reflect mainly the lower powder-to-liquid ratio used for the former application. Alterations in water content will influence the compressive and tensile strength of the cements.

Solubility

During the first 24 hours after mixing, zinc phosphate cements exhibit significant solubi-

lity in water, ranging from 0.04% to 3.3% by weight, presumably due to the continuing setting reaction of the cement. The dissolution rate decreases considerably after this time, when the material has fully set. A high powder-to-liquid ratio also strongly influences the solubility rate of the cements. The ions eluted within the initial setting period are magnesium and small quantities of zinc, and some release of zinc and phosphate ions may occur after completion of setting. Fluoride-containing cements exhibit a dissolution rate of 0.7–1.0% by weight, which occurs over a longer period of time than the dissolution of non-fluoride-containing cements, presumably owing to the interference of the fluoride-releasing mechanism. The solubility of zinc phosphate cements in dilute organic acids, such as lactic or acetic acid, is appreciably higher (20 to 30 times) than that in water. However, the weight of cement dissolved in water and in organic acids, as measured *in vitro*, does not correspond to the disintegration rate of the cement when placed in the oral cavity.

The *in vivo* solubility of the cement is a highly important clinical property, since dissolution of the luting cement may result in plaque retention and subsequent development of primary caries. Additionally, continuous loss of the cement may cause loosening of the orthodontic bands.

Zinc Polycarboxylate Cements

Zinc polycarboxylate (polyacrylate) cement was introduced by Smith in 1968 and at that time represented the new generation of dental cements. This cement was the first dental material developed with adhesive potential to enamel and dentin. The polycarboxylate cements appear to combine the desirable properties of the zinc phosphate and zinc oxide-eugenol cements. The clinical indications for the polycarboxylate cements are similar to those for zinc phosphate cements.

Composition

The zinc polycarboxylate cements are available as powder/liquid formulations. The powder is

based upon components similar to those for the zinc phosphate cement powders (Fig. 11.3), and is mainly composed of zinc oxide with up to 10% magnesium oxide or tin oxide. Silica, alumina, or bismuth salts, and small quantities (4–5%) of stannous fluoride may be incorporated in some brands. The presence of the fluoride in these cements also increases the strength while controlling the setting time. Pigments may also be incorporated to provide a variety of shades.

The manufacturing procedure for the powder involves firing a blend of zinc and magnesium oxides between 900°C and 1000°C for 8 to 12 hours, grinding the sintered mass to the appropriate particle size, and reheating for another 8 to 12 hours.

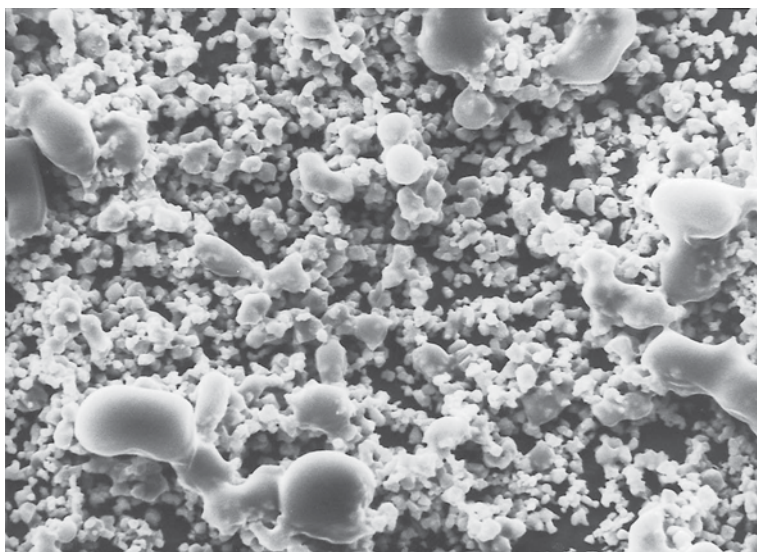


Fig. 11.3 Secondary electron image of the powder particles of a zinc polycarboxylate cement. Original magnification $\times 1000$

The liquid is an aqueous solution of a homopolymer of acrylic acid or a copolymer of acrylic with other unsaturated carboxylic acids such as itaconic and maleic acids. The acid concentration in the liquid is approximately 40% by weight, and the molecular weight of the polyacids varies from 22,000 to 50,000. While this high molecular weight may increase the strength of the cement, undesirable effects such as a short shelf-life and difficulties in manipulation occur because of the relatively high viscosity of the liquid. In some formulations the polyacid is a freeze-dried powder, which is then mixed with the zinc oxide powder and with tap water or distilled water or a solution of NaH_2PO_4 .

Setting Reaction and Structure

Setting of the zinc polycarboxylate cements occurs by an acid-base reaction between the zinc oxide powder and the polycarboxylic acid to form polycarboxylate salts. Upon mixing of the powder and liquid, an initial rapid stage is associated with attack of the powder particles by the acid, which releases zinc and magnesium ions. At the same time, ionization of the polycarboxylic acid takes place. This initial stage is followed by interaction between the carboxyl groups of adjacent polyacid chains and the metal ions to form cross-linked polycarboxylate salts, which act as the cement matrix (Fig. 11.4). The magnesium polycarboxy-

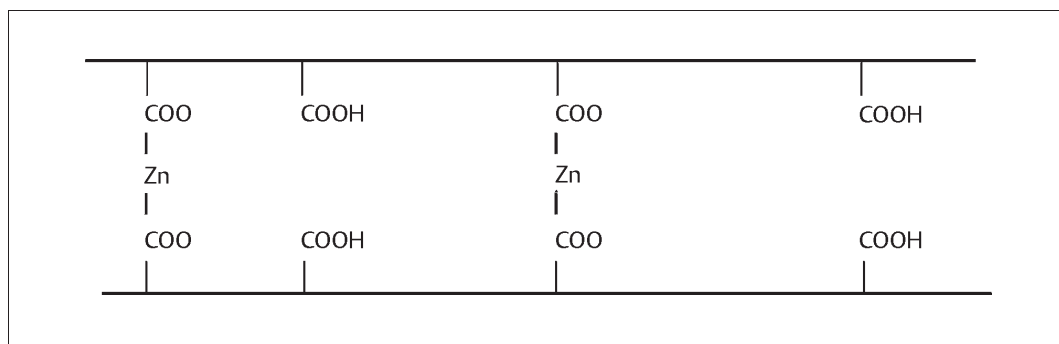


Fig. 11.4 Schematic representation of the chemical structure of polycarboxylate salts formed between polyacrylic chains and zinc ions

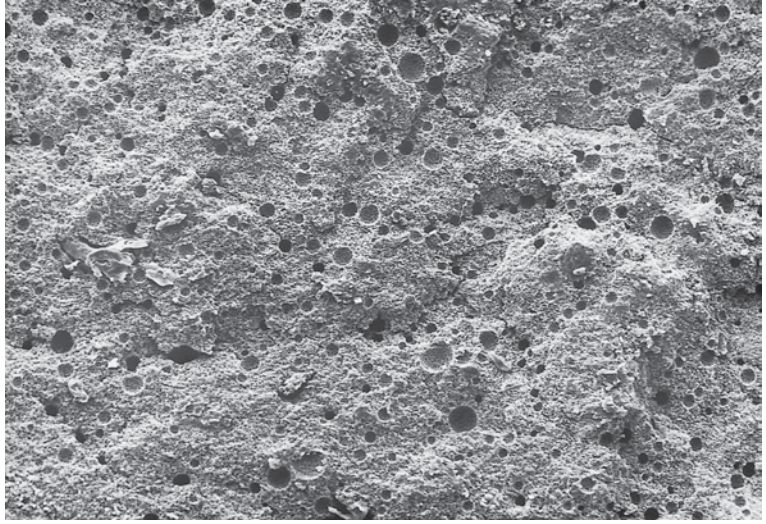


Fig. 11.5 Secondary electron image of porosity in a set (48 hours) zinc polycarboxylate cement. Original magnification $\times 200$

late salts have less hydrolytic stability than the corresponding zinc salts. Thus, a magnesium oxide concentration of up to 10% may yield cements with potential for higher solubility in the oral cavity.

In water-setting polycarboxylate cements, initiation of the acid-base reaction occurs after hydration of the freeze-dried polyacid powder particles. The set cement consists of an amorphous salt matrix in which unreacted and partially reacted zinc and magnesium oxide particles are dispersed. An empirical formula for these salts is: $\text{Zn}_{0.98}\text{H}_{0.004}(\text{CH}_2 \cdot \text{CH} \cdot \text{COO})_{2.0}(\text{H}_2\text{O})_{1.61}$. Both tightly bound water and loosely bound water are present in the set cement. The loosely bound water is considered to act as a plasticizer, causing weakening of the cement.

Working and Setting Times; Manipulative Variables; Film Thickness

In general, the zinc polycarboxylate cements have much shorter setting times than the zinc phosphate cements, which may be considered a potential clinical problem. Mixing of the polycarboxylate cements should be completed rapidly within 30–40 seconds. The working time varies from 2 to 5 minutes at room temperature (23 °C), and the setting time ranges

from 6 to 9 minutes at 37 °C, which is an acceptable range for a luting cement. The setting reaction in water-based formulations proceeds more slowly than in the polyacrylic acid-based products, and thus the setting time is longer. The cement liquid is quite viscous, which can cause difficulty during the mixing procedure and can result in a highly porous material (Fig. 11.5). The powder should be rapidly incorporated into the liquid in large quantities to optimize the working time and setting time. Factors that influence the setting rate include the powder-to-liquid ratio, the powder composition, and the type, concentration, and molecular weight of the polycarboxylic acids.

The working time of the polycarboxylate cements can be extended, as with other cements, by lowering the temperature of the mixing slab and storing the powder in a refrigerator. However, refrigeration of the cement liquid should be avoided, because gelation may occur from the formation of hydrogen bonds. Prolonged storage at room temperature or the absence of moisture may also lead to gelation and thickening of the liquid. The use of a very cold slab is not recommended since it may cause difficulties in the mixing procedure by increasing the viscosity of the liquid.

The cement mixture should be used while it still has a glossy surface appearance. Often, a lower than optimum powder-to-liquid ratio is used in an attempt to produce a thin polycarboxylate paste comparable in viscosity to that

of the more familiar zinc phosphate cement mixture. This procedure should be avoided since it will yield inferior properties for the set cement.

Polycarboxylate cements lack the relatively efficient mixing characteristics of the zinc phosphate cements because of their highly viscous liquids. Although the polycarboxylate cement mixture has a thicker consistency than that for zinc phosphate cement, it flows readily when loaded, yielding an appropriate film thickness of approximately 20 μm . This is because the polycarboxylate cements exhibit pseudoplastic behavior, undergoing shear thinning when pressure is applied during seating of orthodontic bands. A plot of shear stress as a function of strain rate has a decreased slope at high shear rates for a pseudoplastic material, whereas the linear slope remains constant for a material exhibiting newtonian viscosity, such as a zinc phosphate cement mixture. For water-mixed polycarboxylate cements, the initial viscosity occurring immediately after mixing is lower than that of the formulations in which the cement liquid contains polyacrylic acid.

Properties

Strength

Zinc polycarboxylate cements set relatively rapidly, attaining approximately 80% of their final strength within an hour. At luting consistency, the fully set cements at 24 hours after mixing have compressive strengths ranging from approximately 48 to 80 MPa, diametral tensile strengths of approximately 6 MPa and uniaxial tensile strengths ranging from 8 to 12 MPa. The modulus of elasticity of the zinc polycarboxylate cements is between approximately 3 and 6 GPa, which is about half of that of the zinc phosphate cements. These cements are substantially inferior to the zinc phosphate cements in compressive strength, but have slightly higher diametral tensile strength. The strength is improved by using a higher powder-to-liquid ratio when mixing the cement, and by the presence of additives such as alumina and stannous fluoride in the powder. In addition, the polycarboxylate cements exhibit some plastic deformation during

mechanical testing, in contrast to the completely brittle behavior of the zinc phosphate cements. The polycarboxylate cements retain this plastic deformation behavior even after aging, while no adverse effect on their mechanical properties is evident *in vitro* after long-term storage.

Solubility

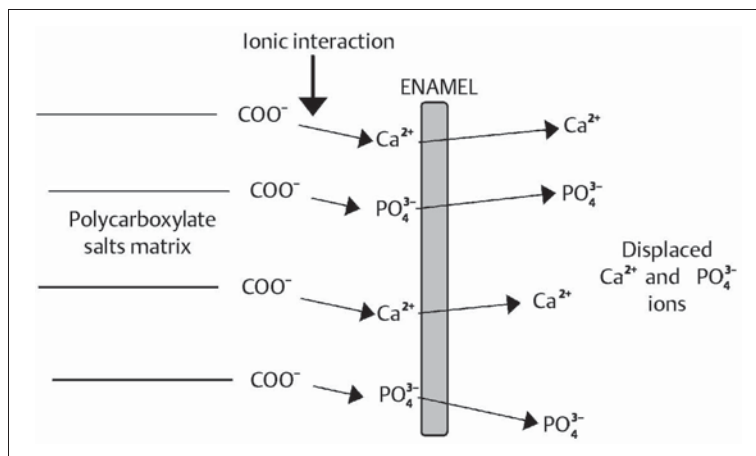
The solubility of the zinc polycarboxylate cements in water is low, ranging between 0.1% and 0.6% by weight. Some products incorporating stannous fluoride exhibit higher solubility because of the fluoride release.

In set cements, dissolution is mostly observed at the unreacted or partially reacted zinc oxide particles rather than in the polycarboxylate salt matrix. Greater dissolution, involving elution of magnesium and zinc ions, has been reported for cements containing copolymers based on maleic acid than for copolymers based on itaconic acid. Polycarboxylate cements have lower resistance to dissolution under acidic conditions. Organic acids such as lactic acid and citric acid markedly increase the cement solubility, depending upon the pH of the environment. In general, polycarboxylate cements have been found to be less susceptible to dissolution in acids than are zinc phosphate cements.

Bonding

An outstanding feature of the zinc polycarboxylate cements is their demonstrated ability to bond to enamel and dentin. While the precise nature of the bonding mechanism to enamel has yet to be established, several theories have been proposed. The polycarboxylic chains may form a chelate with the calcium ions present in enamel and dentin, or they may develop an ionic attraction caused by polyacrylate formation between polyacrylic acid and the hydroxyapatite constituent of enamel and dentin. The calcium and phosphate ions present in the hydroxyapatite may also be displaced by the polyacrylate ions, which then enter the hydroxyapatite structure (Fig. 11.6). This latter bonding mechanism assumes the presence of an intermediate layer consisting of calcium ions, phosphate ions, and polyacrylate ions that forms between the cement and the tooth tissue.

Fig. 11.6 Possible mechanism of adhesion of polyalkenoic acid cements (zinc polycarboxylate and glass-ionomer cements) to tooth enamel



Bonding with the zinc polycarboxylate cements is assured when the surface of the cement has a glossy appearance. This indicates the presence of unreacted carboxyl groups, which are essential for providing bonding between the cement and the tooth tissues.

The *in vitro* cement-enamel tensile bond strength provided by this material has been shown to range between approximately 4 and 6.5 MPa. The much higher bond strength to enamel compared to that for dentin emphasizes the significant role of hydroxyapatite in the adhesion to tooth structure. The actual bond strength attained may be higher than the reported values, since debonding failures

in vitro are generally cohesive, where the tensile strength of the polycarboxylate cement has been exceeded. Thus, commercially available agents that are recommended for enamel pretreatment to improve the bond strength to polycarboxylate cements might not be effective. *In vivo* bond strength values to polycarboxylate cements may be much lower than *in vitro* values, ranging from approximately 2 to 3 MPa.

It should be noted that these cements are capable of bonding with surfaces of metallic restorations, prostheses, and appliances, particularly nickel-chromium, silver-palladium, and stainless steel alloys.

Glass-Ionomer Cements

Background and Applications

The glass-ionomer cements were developed by Wilson and Kent in the early 1970s, and were designed to combine the strength and fluoride release potential of (the now obsolete) silicate cements with the adhesive efficiency of the zinc polycarboxylate cements. The glass-ionomer cement is formed by mixing an ion-leachable glass powder similar to that for the silicate cements with polyalkenoic acids similar to those in the polycarboxylate cement liquids.

Glass-ionomer cements are used in a wide range of clinical applications, such as restorations, pit and fissure sealants, and cavity liners,

along with their use as luting agents for inlays and crowns. The glass-ionomer cements became popular in orthodontics during the late 1980s. The higher survivorship rate for glass-ionomer cements compared to zinc phosphate cements, combined with their fluoride release potential, made them highly attractive for band cementation. Moreover, some glass-ionomer cements have been recommended as an alternative to adhesive resins in orthodontic direct bracket bonding (Chapter 5). Bonding brackets with glass-ionomer cements has the advantage of avoiding an enamel etching procedure, which practically results in elimination of the mineral loss that occurs during debonding when adhesive resins are used.

Furthermore, use of the glass-ionomer cements may minimize the potential risk of subsurface demineralization that is typically observed at the periphery of brackets bonded with adhesive resins. However, the prolonged setting time and concomitant slow development of strength, along with concern about the initial sensitivity of glass-ionomer cements to moisture contamination, may be considered disadvantages for the orthodontic use of these materials.

The development of improved glass-ionomer cements is an active area of research, and manufacturers are continuously modifying products to improve their setting characteristics and properties. Light-cured resin-modified glass-ionomer cement formulations for use in liner/base and restorative applications have been recently introduced. The problem of incomplete polymerization at sites inaccessible to the photocuring light has stimulated the introduction of self-cured resin-modified luting cements.

The more rapid setting reaction, the improved physical and mechanical properties, and the higher bond strength to enamel of the resin-modified glass-ionomer cements, compared to the conventional formulations, make them very attractive materials for orthodontic applications. Many light-cured and chemically cured resin-modified glass-ionomer cement products have been recently introduced for use in bonding. Table 11.1 provides a list of glass-ionomer cements marketed for orthodontic applications.

Composition

Glass-ionomer cements have been developed as powder-liquid systems in hand-mixed or encapsulated formulations.

The powder component consists of calcium fluoroaluminosilicate glass particles; the fluoride content is high (10–23% by weight). The glass particles are partially dissolved during

Table 11.1 Glass-ionomer cements used in orthodontic bonding

Conventional Glass-Ionomer Cements	Light-Cured Resin-Modified Glass-Ionomer Cements	Chemically Cured Resin-Modified Glass-Ionomer Cements	Glass-Ionomer Cements for Orthodontics
*Ketac-Cem (l) Premier/ESPE-Premier	Photac-Fil (r) ESPE	Advance (l) Dentsply/Caulk	*Fuji Ortho GC International
*Fuji I (l) GC International	Fuji II LC (r) GC International	Fuji Duet (l) GC International	*Fuji Ortho LC GC International
Ketac-Bond (b) Premier/ESPE-Premier	Vitremer (r) 3M	Vitremer Luting (l) 3M Unitek	
Chem-Fil (r) ESPE	Variglass VLC (r) Vivadent	*Multi-Cure Glass Ionomer Orthodontic Band Cement (l) 3M Unitek	
Ketac-Fil (r) Premier/ESPE-Premier	Geristore (r) Den-Mat		
Fuji II (r) GC International	Fuji Lining LC (b) GC International		
*Aqua-Cem (l) Dentsply/DeTrey	Zionomer (b) Den-Mat		
GlasIonomer (l) Shofu	Vitrabond (b) 3M Unitek		

*Cements designated with an asterisk are recommended by the manufacturer for orthodontic application. Codes for product use: (l), luting; (r), restorative; (b), liner/base

the setting reaction, releasing sodium, calcium, aluminum, and silicate ions into the liquid solution. The ability of the glass composition in the powder to react with the liquid and form a cement is regulated by the critical $\text{SiO}_2/\text{AlO}_3$ ratio. For a glass-ionomer cement of appropriate setting time and desirable strength, this ratio should be 2.0.

The manufacturer initially forms the glass composition for the cement powder particles by fusing quartz, alumina, calcium fluoride, cryolite (Na_3AlF_6), aluminum fluoride, and aluminum phosphate between 1100°C and 1300°C . The resulting glass is cooled in water and ground to yield a frit (particles of glass). The desired particle size depends upon the prospective use of the cement. Small particle-size glasses ($\sim 20\ \mu\text{m}$) are intended for luting cements to obtain a higher powder-to-liquid ratio, rapid setting, and the desired film thickness. Trace amounts of strontium, barium, and lanthanum ions are used to provide radiopacity, while the incorporation of corundum (Al_2O_3) and rutile (TiO_2) crystalline filler particles results in cements with improved flexural strength.

The powder of the resin-modified glass-ionomer cements consists of either the glass composition used for the conventional glass-ionomer cements or a strontium aluminofluorosilicate glass; a barium aluminosilicate glass is also incorporated in some products. The differences in the glass compositions of the powders account for some of the variations in the setting reactions and the properties of the commercial products.

The liquid component of the originally introduced glass-ionomer cement formulation was an aqueous solution of polyacrylic acid. This solution was found to be unstable, with gelation

occurring after extended storage times. Subsequent liquid components consisted of polyacrylic, maleic, or other polycarboxylic acid copolymers, containing approximately 5% by weight of itaconic acid (Fig. 11.7). The problem of a slow setting reaction for the original glass-ionomer cement formulation was overcome by the incorporation of the optically active *D* (+) isomer of tartaric acid as a reaction rate-controlling additive to the liquid component. This additive was found to decrease the setting time and increase the strength of the cement, while having no effect on the working time.

In some glass-ionomer cement formulations, vacuum-dried polyacrylic acid is also incorporated into the glass powder. Mixing of glass-ionomer cements is performed with tap water or distilled water or with an aqueous solution of tartaric acid. Water-hardening glass-ionomer cements are less viscous than the conventional formulations, and have unlimited shelf-life and prolonged setting time.

Significant alterations have been made in the liquid component of the light-cured resin-modified glass-ionomer cements. The most prominent changes are the replacement of water by a water-HEMA (hydroxyethyl methacrylate) mixture and the incorporation of photoinitiators and/or chemical initiators for free-radical polymerization. In some products, methacrylate-based monomers, *i.e.*, Bis-GMA, TEGDMA, and UDMA (see Chapter 9), are added to the polyacrylic acid solution; methacrylate-functionalized polyacrylic acids may also be used (Fig. 11.8). Variations in the water concentration and the acidity of the liquid for resin-modified glass-ionomer cements have been reported and appear to influence the acid-base setting reaction.

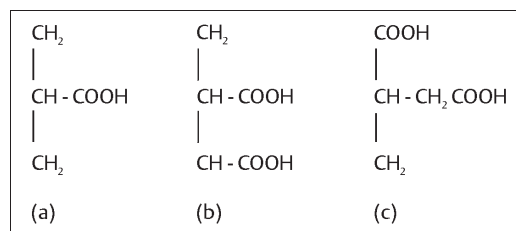


Fig. 11.7 Schematic representation of the chemical structure of polyalkenoic acids used in glass-ionomer cements: (a) acrylic, (b) maleic, (c) itaconic

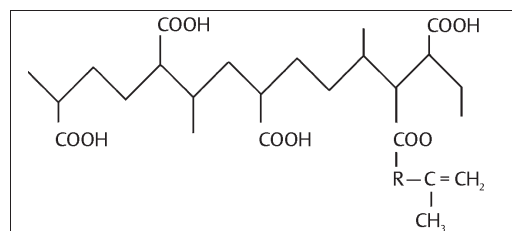


Fig. 11.8 Schematic illustration of a polyacrylic acid, methacrylate-functionalized chain used in resin-modified glass-ionomer cements

Setting Reaction and Structure

The setting reaction of the conventional glass-ionomer cements can be represented as an acid (liquid)-base (powder) reaction leading to the formation of polycarboxylate salts that comprise the cement matrix. The reaction occurs in three distinct stages: dissolution, gelation, and final hardening (Fig. 11.9).

During the initial reaction or dissolution stage, the carboxyl (COOH) groups are dissociated to carboxylate groups (COO⁻) and hydrogen (H⁺) ions. The positively charged hydrogen ions attack the surface layer of the glass particles, releasing calcium and aluminum ions in the form of fluoride complexes. The calcium ion concentration rises more rapidly than that of the aluminum ions in the cement sol. Simultaneously, as the ionization reaction continues, the polyacrylic chains assume a more linear format, allowing the commencement of gelation, which represents the second reaction stage.

During the gelation stage, the more mobile and readily available calcium ions are complexed with the carboxyl groups, and a weak ionic cross-linking is formed, which corresponds to the initial setting of the cement that is observed clinically. At this initial setting, moisture contamination may be detrimental to the cement, disturbing the formation of the matrix of reaction products and causing a chalky and porous appearance.

As the setting reaction continues, Al³⁺ ions are increasingly deposited in the matrix, leading to a three-dimensional, highly cross-linked

calcium-aluminum carboxylate gel that corresponds to the final stage of cement hardening. Gradual hydration of the salt matrix and a rapid increase in the cement strength occur during this reaction phase. The reaction rate in these materials is governed by the temperature, powder-to-liquid ratio, powder particle size, free fluoride ions, and the presence of tartaric acid. The final set structure is described as a complex composite consisting of unreacted and partially reacted glass particles surrounded by a siliceous hydrogel and embedded in a cross-linked calcium and aluminum polycarboxylate salt matrix. The microstructure of a conventional glass-ionomer cement having a luting consistency is shown in Fig. 11.10.

The light-cured resin-modified glass-ionomer cements are dual-setting reaction cements. Upon mixing of the powder and liquid components, the previously described acid-base reaction again takes place, but now accompanied by a free-radical polymerization mechanism, similar to that found in resin composites (Chapter 9). Exposure of the cement to the curing light may retard the acid-base reaction rate. When a chemically activated free-radical polymerization approach is employed, the polymerization process is initiated by mixing the powder and liquid. The latter resin-modified glass-ionomer cement formulations are characterized as “dual-cured” products. The setting of these chemically cured resin-modified glass-ionomer cements thus occurs by an acid-base reaction and free-radical polymerization initiated upon mixing the powder and liquid. The polymerization reaction in these

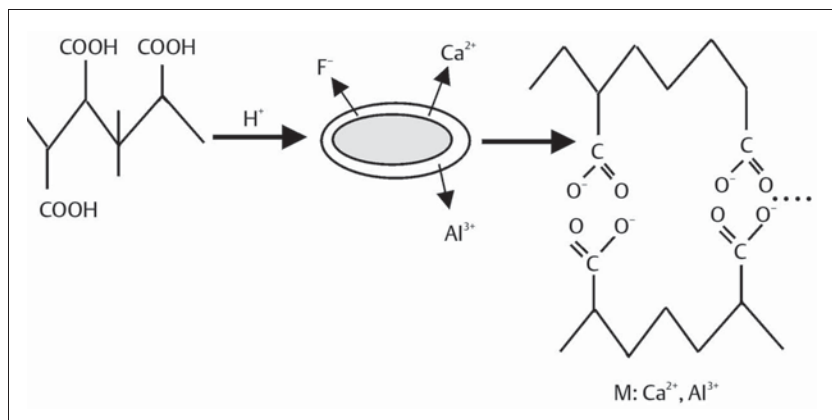


Fig. 11.9 Schematic illustration of the three setting reaction stages and the formation of polycarboxylate salts in conventional glass-ionomer cements. The metal ions (M) participate in formation of the cross-linked matrix (see also Fig. 11.11)

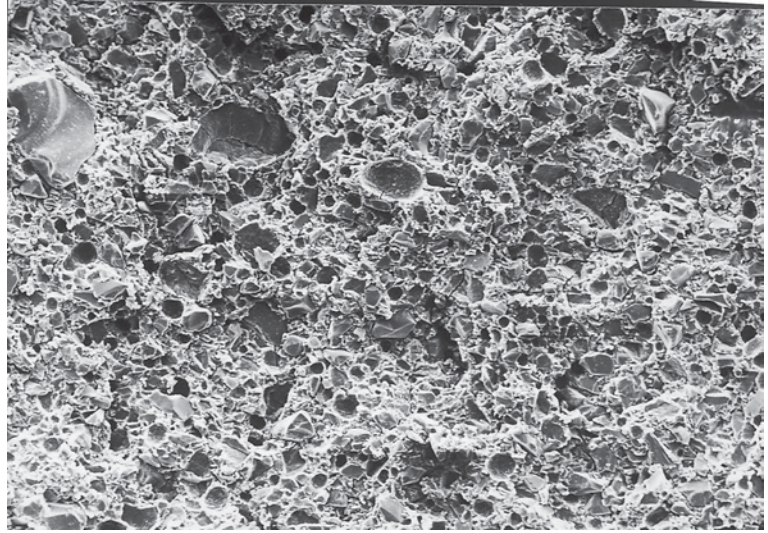


Fig. 11.10 Secondary electron image of a conventional glass-ionomer cement having a luting consistency. Original magnification $\times 200$

materials involves copolymerization of the HEMA with the polymer side chains, homopolymerization of the HEMA, or homopolymerization of the functional groups in the side chains (Fig. 11.11).

The final hardening and strengthening of the glass-ionomer cements is enhanced by the formation of the polycarboxylate salt matrix. It should be noted that the acid-base reaction mechanism that leads to the salt formation has not been identified in all of the commercially available formulations of the resin-modified glass-ionomer cements. Low water concentration, insufficient reactivity of the glass particles, and low acidity of the cement liquid are major factors that can contribute to inhibition of the acid-base reaction. Using these three criteria, some commercial products do not fulfill the requirements for being characterized as true glass-ionomer cements.

The degree of conversion and possible polymerization defects may be an important consideration with the resin-modified glass-ionomer cements. The percentage of remaining carbon-carbon double bonds ($C=C$) after setting of these cements has been found to range between 33% and 55%. In addition, substantial setting stresses are developed within resin-modified glass-ionomer cements during exposure to the curing light, whereas such stresses are negligible in conventional glass-ionomer cements (Fig. 11.12). No information is currently

available on the impact of the degree of conversion, setting stresses, and possible polymerization defects on the clinical performance of the resin-modified glass-ionomer cements.

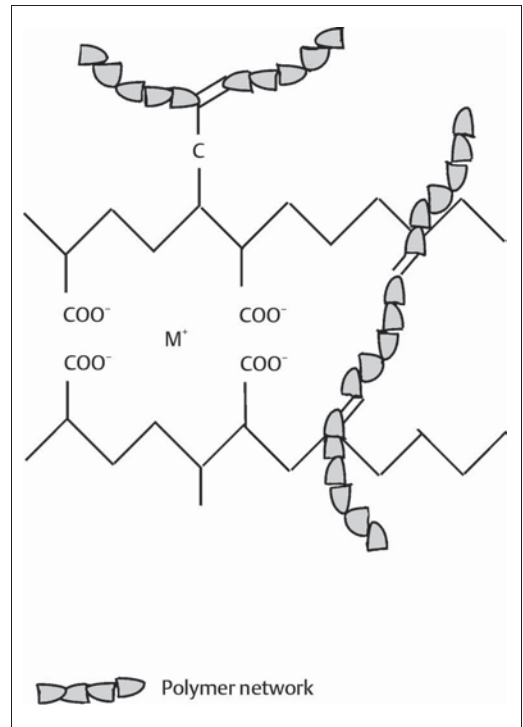


Fig. 11.11 Schematic illustration of the structure of a resin-modified glass-ionomer cement

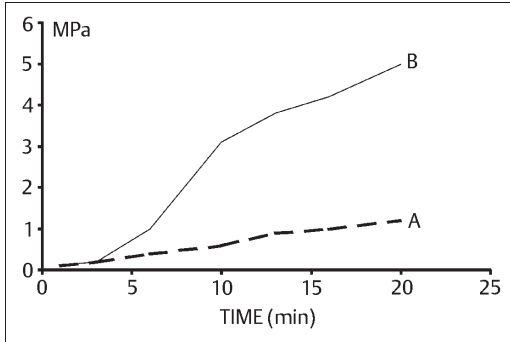


Fig. 11.12 Stresses developed during setting in a conventional (curve A) and a light-cured resin-modified (curve B) glass-ionomer cement

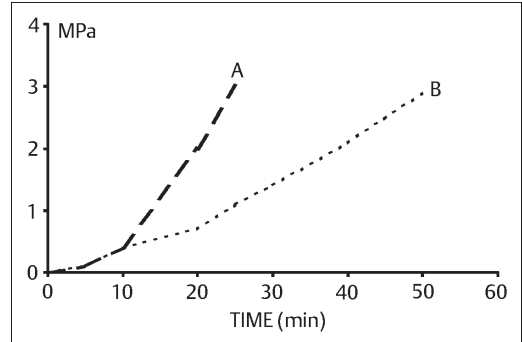


Fig. 11.13 Plot of stress as a function of time during setting for polyacrylic acid-containing (curve A) and water-based (curve B) glass-ionomer cements

Working and Setting Times; Manipulative Variables; Film Thickness

The luting glass-ionomer cements have extended working times (3 to 5 minutes) and relatively short setting times (5 to 9 minutes), compared to the other types of glass-ionomer cements. However, the setting time for the luting glass-ionomer cements is still long relative to those of the zinc polycarboxylate and zinc phosphate cements. The water-based glass-ionomer cements have longer working and setting times (Fig. 11.13) compared to the polyacid acid-containing cements. The amount of tartaric acid in the liquid component greatly influences the working and setting times, which are prolonged by mixing the powder and liquid components on a cold slab.

The rheological properties of the luting glass-ionomer cements enable the formation of a film ranging from 25 to 35 μm in thickness. The pseudoplastic characteristics of the glass ionomer cements are decreased by an increase in the powder-to-liquid ratio and delayed seating of the band or bracket. Since these cements are highly sensitive to the mixing procedure, often the appropriate film thickness cannot be attained *in vivo*.

Resin-modified glass-ionomer cements have longer working times and undergo rapid setting after light-curing. The desirable film thickness of these cements for luting applications may be obtained with a lower powder-to-liquid ratio than that recommended by the manufac-

turers to achieve the consistency of restorative cements.

The proper technique should be followed to achieve successful results for luting with a glass-ionomer cement. The enamel surface should first be pumiced, rinsed, and dried without any desiccation taking place; the use of conditioning agents does not appear to improve the retention of the appliance to enamel. The powder should be incorporated into the liquid in large portions, and rapid spatulation for 10 seconds is suggested; the usual working time is up to 20 seconds.

Mixing on a large, cold glass slab (temperature above the dew point) with a flexible spatula is recommended, and cementation should take place immediately while the mixture still has a glossy appearance. Use of a cold slab allows an increase in the powder-to-liquid ratio during mixing, and a smaller film thickness can be obtained. For encapsulated glass-ionomer cement formulations, the mixing time with the triturator influences the handling properties, the film thickness, and the physical and mechanical properties.

Prior to seating of the band or the bracket, varnish should be applied to the adjacent uncovered enamel surface to assure the easy removal of excess cement. Following cementation, the band or bracket should be maintained in place during the initial hardening period; the excess cement may be carefully removed. The margins of the setting cement should be protected from moisture contamination with a varnish or by applying a light-cured

bonding agent to prevent softening and subsequent erosion of the cement surface.

A similar procedure may be followed with the resin-modified glass-ionomer cements. Irradiation with the visible light source should be performed immediately after placement of the cement.

Properties

Strength

Although the luting glass-ionomer cements exhibit excellent setting characteristics, they have the lowest strength among the different types of glass-ionomer cements. This is attributed to the significantly lower powder-to-liquid ratio utilized in mixing. While the strength of these materials is developed rapidly after mixing, it continues to increase for a long period of time that may exceed one month.

The compressive strength of the luting glass-ionomer cements ranges between 90 and 140 MPa, which exceeds values for zinc phosphate and zinc polycarboxylate cements. The diametral tensile strength of the luting glass-ionomer cements is slightly higher (6.5–8 MPa), and the uniaxial tensile strength significantly higher (6–8 MPa), when compared to other types of luting cements. These glass-ionomer cements also exhibit some plastic deformation during mechanical testing, in a similar manner to that for the zinc polycarboxylate cements.

The modulus of elasticity of fully set glass-ionomer cements is higher than that of the zinc polycarboxylate cements and about one-half that of the zinc phosphate cements. Thus, the glass-ionomer cements demonstrate more elastic deformation than the zinc phosphate cements and less than the zinc polycarboxylate cements when subjected to the same stress. The elastic deformation is higher for glass-ionomer cements that have not completed the setting reaction. As these cements become progressively more rigid, their viscoelastic behavior is diminished.

The flexural strength (9–20 MPa) and fracture toughness are higher for glass-ionomer cements than for all other types of luting cements. Although the glass-ionomer cements are inappropriate for clinical applications where high stresses may be encountered, they are frequently used for class V restorations.

Solubility

The solubility in water of the fully set glass-ionomer cements is considerably lower than that of zinc polycarboxylate and zinc phosphate cements. However, their early susceptibility to moisture within 4 to 10 minutes after the start of mixing is very high, with a rapid decrease occurring over the following 24 hours as the cement sets. Thus, early protection of the cement surface with a hydrophobic agent may be necessary to avoid disruption of the setting process by water. The majority of the species eluted are non-matrix-forming ions, such as sodium and fluoride ions, and silicic acid.

When exposed to acid attack, glass-ionomer cements exhibit higher erosion than that in water, and matrix ions are lost with the formation of porosity (Fig. 11.14). However, the erosion rate noted is low relative to that for zinc polycarboxylate and zinc phosphate cements. The severity of erosion depends on the pH of the environment, and it has been found that erosion is initiated at pH 4. The extent of erosion increases with time after mixing of the glass-ionomer cement.

In general, the resin-modified glass-ionomer cements demonstrate superior compressive, uniaxial tensile, and diametral tensile strength compared to the conventional glass-ionomer cements. The former cements have greater flexural strength and fracture toughness, and are more resistant to permanent deformation and dissolution in wet environments, even during the early setting stage. A more rapid rate of strength development for these materials may be attained by photopolymerization, which presumably accelerates the setting process. Although significant improvements in properties have taken place with the development of resin-modified glass-ionomer cements, the physical and mechanical properties of these materials are inferior to those of the resin composites. Table 11.2 compares the mechanical properties of various cements.

Bonding

The use of resin composites as orthodontic bonding agents requires some loss of enamel during etching and debonding (Chapter 5), and the debonding procedure is relatively laborious and not risk-free. The basic mechan-

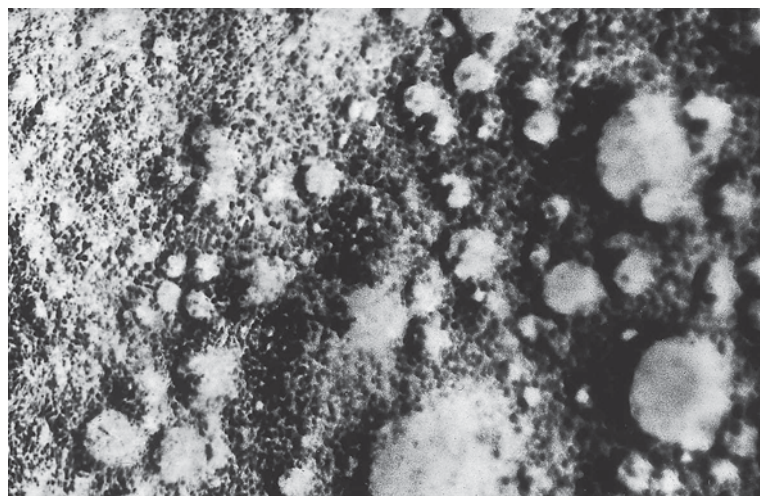


Fig. 11.14 Appearance of a glass-ionomer cement after immersion in lactic acid (pH 4) for one week. A destroyed cement matrix and considerable porosity are observed. Light microscope, bright field, $\times 50$

ism for bonding glass-ionomer cements to enamel is essentially the same as that for bonding zinc polycarboxylate cements to enamel.

Prior to application of the glass-ionomer cement, the enamel surface for bonding may be conditioned (etched) with an aqueous solution of polyacrylic acid having a concentration in the range of 10–40%.

Bond strength values reported for glass-ionomer cements exhibit a large variation (approximately 3–7.5 MPa) in shear stress, depending upon the product tested. These

values are influenced principally by the cohesive strength of the cements, since *in vitro* failures for bonded brackets generally involve cohesive fracture through the adhesive, leaving a layer of the material on the enamel (Fig. 11.15). Removal of glass-ionomer cements can be achieved by using a curet, without causing an adverse effect on the enamel integrity. In general, the values of bond strength for the glass-ionomer cements are lower than those for the adhesive resins and higher than those for the zinc phosphate cements.

Table 11.2 Properties of three major types of cements

Properties	Zinc Phosphate Cements	Zinc Polycarboxylate Cements	Glass-Ionomer Cements (luting consistency)
Working time (min)	3–6	2–5	3–5
Setting time (min)	5–9	6–9	5–9
Film thickness (μm)	20	20	25–35
Compressive strength (MPa) ^a	80–140	48–80	90–140
Tensile strength (MPa) ^a	5–7	8–12	6–8
Diametral tensile strength (MPa) ^a	5	6	6.5–8
Modulus of elasticity (GPa) ^a	9–13	3–6	3.5–4
Solubility (wt%) ^a	0.04–3.3	0.1–0.6	1

^aValues after 24 hours.

Fig. 11.15 Photograph of the *in vitro* failure site for a bracket bonded with glass-ionomer cement, showing cohesive fracture through the adhesive where a layer of the material remains on the enamel



The ability of glass-ionomer cements to bond to base metal alloys is an important feature of these materials. The bond between the glass-ionomer cements and enamel is superior to that between these cements and stainless steel bands and brackets. This may explain the failure mode of cements during debanding/debonding, which essentially involves adhesive fracture at the band-glass ionomer or bracket-glass ionomer interface. However, some cases of failure patterns during debonding that included cohesive fracture at the enamel-glass ionomer interface and at the stainless steel bracket-glass ionomer interface have been reported. These observations are attributed to additional mechanical retention provided by the bracket base design, in contrast to the relatively smooth inner surface of the band.

Resin-modified glass-ionomer cements appear to provide significantly higher bond strength than the conventional glass-ionomer cements and a decreased probability for bond failure. The lower frequency of cohesive and adhesive enamel failures reported for these cements indicates that the greater strength of the resin-modified glass-ionomers may result in a superior bond. Although the bonding mechanism of the resin-modified glass-ionomer cements with dentin has been studied extensively, limited information is available about the bond established with enamel. In addition,

the longevity of the bonds developed by these recently developed cements has not been established with suitable *in vivo* studies. Enamel pretreatment with aqueous solutions of polyacrylic acid or bonding agents is recommended when using resin-modified glass-ionomer cements.

Fluoride Release and Anticariogenic Potential

Fixed orthodontic therapy presents a high and continuous cariogenic challenge, as discussed in Chapter 6. The development of enamel demineralization and the formation of white spot lesions adjacent to bands/brackets have been reported repeatedly. Glass-ionomer cements are thought to act as a reservoir of fluoride, providing a possible means to minimize the potential of subsurface enamel demineralization. The capacity of all types of glass-ionomer cements, and particularly the luting cements, for releasing fluoride ions has been well established in a variety of *in vitro* studies. In these studies, the initially elevated rate of fluoride release is attributed to higher elution occurring before the cement has set. A gradual decrease in the amount of fluoride release is seen during the setting process for the cement, finally attaining a low constant level. The fluoride release is

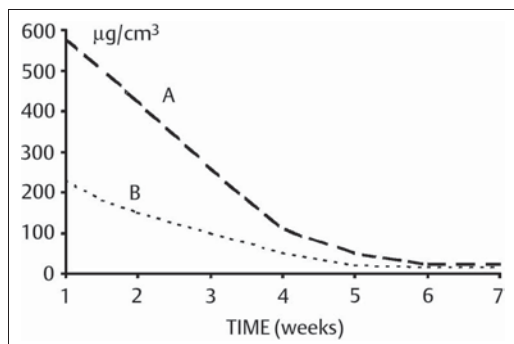


Fig. 11.16 Profiles of fluoride release rate for a conventional glass-ionomer cement (curve A) and a resin-modified glass-ionomer cement (curve B)

more pronounced in acidic than in neutral environments. It is worth noting that the fluoride release from resin-modified glass-ionomer cements has a relatively constant rate, characterized by a substantially lower initial ion elution compared to the other types of glass-ionomer cements (Fig. 11.16). The latter may be associated with the higher resistance to dissolution at the initial setting stage demonstrated by the resin-modified glass-ionomer cements. Generally, the elution of fluoride from glass-

ionomer cements is achieved through diffusion and/or erosion processes.

Salivary fluoride levels during orthodontic therapy that involves appliances bonded with glass-ionomer cements are increased the day following insertion. However, this initial elevation is eliminated after a period of four weeks. Also, an elevated fluoride concentration has been reported in dental plaque adjacent to orthodontic brackets and bands bonded with glass-ionomer cement. Nonetheless, fluoride uptake from glass-ionomer cements into enamel has not been documented. *In vitro* studies have shown that the demineralization occurring under and around orthodontic bands and brackets bonded with glass-ionomer cements is considerably lower than that found with zinc phosphate cements and resin adhesives. *In vivo* studies have also established the substantial reduction in frequency of white spot lesions. However, no total protection for the extended period of active orthodontic treatment is achievable. The inhibition of demineralization adjacent to orthodontic bands and brackets is most likely due to localized fluoridation of the potentially cariogenic environment. The relatively anticariogenic performance of the glass-ionomer cements may be beneficial, particularly in patients at high risk for caries.

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12 Impression Materials

William M. Johnston



An impression obtained with a polyvinylsiloxane impression material

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Introduction

A dental impression material is used to make a mold that has the negative dimensions of the surfaces of a patient's oral structures. The purpose of the impression is the formation or establishment in the ensuing "positive" model (typically prepared from a dental gypsum product) of the proper physical dimensions, shapes, and spatial relationships of these structures. Most commonly, an impression material is prepared in a low-viscosity state, placed and formed against the oral structures before a significant increase in the viscosity of the material occurs, then removed from the patient's mouth and used to form the model or to relate models of opposing arches. This increase in viscosity, referred to as setting, can be due to the physical change of cooling or to a chemical reaction. The combination of properties before, during, and after setting determines the suitability of the impression material for each clinical situation.

Materials used to make an impression are usually polymers (e.g., alginate hydrocolloid and polyvinylsiloxane), although some brittle ceramic materials (e.g., dental plaster and zinc oxide-eugenol) may also be used for limited applications. The properties of polymers are dependent upon many factors, but the major factors include the nature of the molecular components and the manner in which these components are bound to one another (Chapter 1). Since changes in molecular binding occur during a setting process, changes in properties accompany setting that are important for successful use of the impression material in the clinic and laboratory. The approach of this chapter is to present some fundamental physical and chemical characteristics of impression materials that are potentially useful to the orthodontist, and then to present the important clinical properties for the ideal impression material with comparisons to available impression materials.

Classes of Impression Materials

The two general classes of impression materials for use in orthodontics consist of those materials that can experience only minimal elastic deformation after setting and those that, after setting, can undergo the large elastic deformations required to remove the impression material over the crowns of all teeth. However,

this latter class, which comprises polymeric materials, can demonstrate significant viscous deformation and is more completely described as *viscoelastic* (Chapter 1). Handling of these materials in a manner that minimizes viscous deformation after setting will promote their successful use clinically.

Thermoplastic Bite Impression Materials

In general, a desirable property of dental impression materials is sufficient elasticity after setting, as discussed more completely below. For example, adequate registrations of the relationship of opposing arches can be removed from the occlusal surfaces of the teeth with minimal deformation. Consequently, bite impression materials require only sufficient elasticity to withstand separation from the occlusal surfaces of teeth. These materials do not require the ability to recover elastically from the large deformations that occur during withdrawal past undercuts on teeth. Since a

thermoplastic polymer transforms from a low-viscosity moldable condition to a high-viscosity state with a decrease in temperature through its glass transition range (Chapter 1), bite registration materials are necessarily thermoplastic polymers whose glass transitions occur slightly above mouth temperature. Rosin, resins, and waxes are thermoplastic polymers that, when combined with appropriate filler particles, can be formulated into convenient bite registration materials. Simple heating of these materials only to a temperature that makes them sufficiently fluid to capture the

occlusal registrations of teeth in opposing arches, followed by cooling to mouth temperature, are required for their use. Clinical use of an excess amount may cause the impression

material to flow into an undercut, with subsequent unwanted plastic deformation or fracture upon removal from the mouth.

Alginate Hydrocolloid

Water, potassium alginate, and calcium sulfate dihydrate react to form a calcium alginate gel that is insoluble in water, and thereby produce a viscoelastic material that has found extensive use as the principal component of an impression material used to obtain orthodontic study models. A substantial amount of filler, with some disinfectant, setting-time modifiers, and chemicals that counteract the inhibiting effect of the gel on the setting of gypsum, are used to provide acceptable clinical properties of this irreversible hydrocolloid impression material. All ingredients except the water are in powder form, and are mixed by the manufac-

turer with a glycol to prevent the small powder particles from becoming harmful dust that might be inhaled as the powder is dispensed. A list of the powder components and their purposes is provided in Table 12.1. Mixing of this powder with adequate water to provide the appropriate initial viscosity starts the setting chemical reaction, forming a gel that loosely contains the excess water. The sequence of reactions associated with the formation of the alginate gel is provided in Table 12.2. The properties of this alginate impression material are dependent on the distribution of the sizes of the powder particles in the mix, thus requiring

Table 12.1 Components of an alginate impression material powder and their functions

Components	Function
Diatomaceous earth or other filler	Control consistency before setting, and flexibility after setting
Potassium alginate and calcium sulfate	Form alginate gel
Potassium sulfate or other gypsum-modifiers	Counteract the inhibiting effect that the set impression has on the setting of gypsum
Sodium phosphate	Initially prevents the calcium ions from reacting, thus extending working time
Ammonium salts and chlorhexidine	Provide disinfection
Glycols	Render the powder dustless
Other	Provide taste and color

From Craig, 1997

Table 12.2 Sequence of reactions in the formation of an alginate impression

(a) Reaction to delay formation of Ca alginate:
$3\text{CaSO}_4 + 2\text{Na}_3\text{PO}_4 \xrightarrow{\text{H}_2\text{O}} \text{Ca}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{SO}_4$
(b) Reaction to form viscoelastic alginate rubber:
$\text{K alginate} + \text{CaSO}_4 + \text{H}_2\text{O} \rightarrow \text{Ca alginate} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ (sol) (gel)

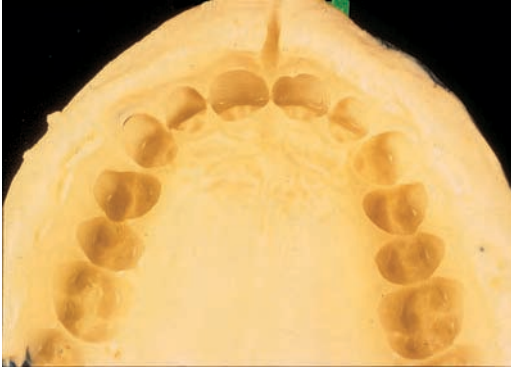


Fig. 12.1 An impression obtained with an alginate hydrocolloid impression material

Rubber Impression Materials

Synthetic oligomers of various molecular compositions and sizes are supplied for use as dental impression materials. Oligomers are long-chain organic molecules that have reactive groups capable of further molecular binding. These oligomers are viscous fluids that can polymerize further through the processes of chain lengthening and cross-linking to form a viscoelastic solid rubber. Polymerization reactions are exothermic, and dimensional contraction of the impression material occurs as a direct result of the increase in density during setting and from cooling after it is removed from the patient's mouth.

The molecular composition of the oligomer determines its basic chemical and physical properties; however, these properties are susceptible to effects of the molecular size of the oligomer. When comparing oligomers of identical molecular composition, the smaller the size of the oligomer, the lower is its viscosity before setting and the greater the dimensional contraction during polymerization. Thus, the light-bodied impression materials, with their smaller oligomer size, register surface detail more readily and tend to displace soft tissue less than their medium-bodied or heavy-bodied counterparts. The light-bodied impression materials may also contain a smaller amount of filler particles. However, the light-bodied materials contract to a greater degree on polymerization and should be used sparingly, only where needed for improved re-

a thorough mixing of the powder prior to dispensing from a large container. The properties of the set material are also highly dependent on the powder/water ratio used to prepare the mix. Precise measurement of the powder and water components is required to assure proper handling characteristics, little dimensional change during setting, and optimal resistance to plastic deformation upon removal from the patient's mouth. After setting, water is easily exchanged into or out of the gel, with resultant changes in dimensional accuracy, so immediate pouring of the model is indicated. Figure 12.1 shows an example of an alginate impression.

gistration of undisturbed surface detail. A compatible heavy-bodied impression material then completes the bulk of this dual-material impression and results in less overall dimensional contraction upon setting. When improved surface detail is not required, a single medium-bodied material can be used to obtain the entire impression, although greater dimensional contraction on setting can result.

Polysulfide Rubber

Mercaptan oligomer polymerizes by a condensation or step-growth process to form a viscoelastic polysulfide rubber. The hydrophilicity of mercaptan allows this material to wet the surfaces of moist oral structures and reduces the possibility of formation of air bubbles at the impression surface. Lead dioxide is the component that is usually incorporated to react with the hydrogen sulfide groups of the mercaptan oligomer and facilitate the condensation polymerization, and this ingredient can leave a dark stain on clothing and other materials with which it comes in contact. The dimensional contraction that occurs during the polymerization of polysulfide rubber requires using this material at minimal thickness, and therefore a custom-made tray is employed. The cross-linking chains that form in the polysulfide rubber are long relative to the lengths of these chains in other synthetic rubber impression

Table 12.3 Components of polyvinylsiloxane impression pastes and their functions

Component	Function
Base siloxane oligomer	To provide inherent chemical and mechanical properties in the set material
Oligomer with terminal vinyl groups	To react with the base oligomer to form a cross-linked elastomer
Platinum acid catalyst	To catalyze the polymerization reaction
Filler	To improve the clinical handling characteristics

From information in Craig, 1997

materials and are not as effective in preventing viscous flow upon removal of the material from the patient's mouth. Water is the condensation product that results from the polymerization of mercaptan, and the release of this unbound water can significantly affect dimensional accuracy over time after setting. Therefore, immediate pouring of the model is indicated. Its bad odor and tendency to flow down a patient's throat promote poor patient acceptance of the polysulfide impression material. The disadvantages usually eliminate this material for use in orthodontics, although its relatively low cost results in substantial clinical usage for other dental applications.

Silicone Rubbers

Dental silicone impression materials are available in two different chemical forms. Each is inherently hydrophobic and, if unmodified as the condensation silicone materials are currently supplied, they require a clean and dry field if surface imperfections are to be avoided. However, the addition type can be successfully modified to make this material hydrophilic.

Condensation Silicone Materials

These materials polymerize by a step-growth process and form alcohol as the condensation product. Liberation of the alcohol can quickly affect the dimensional accuracy of the set material, and immediate pouring of the model is indicated. The hydrophobic nature of these materials after setting increases the difficulty of pouring a stone model with no surface imperfections. These disadvantages usually eliminate this material from use in orthodontics.

Addition Silicone Materials

The combination of oligomers with silane groups and those with vinyl groups will polymerize in the presence of platinum to form a highly elastic and stable polymer often referred to as polyvinylsiloxane. A list of components for polyvinylsiloxane impression material and their functions is provided in Table 12.3. Incorporation of a surfactant or the inclusion of hydrophilic groups on the oligomer, or both strategies, can be employed to make the addition silicone hydrophilic. These materials tend to liberate some hydrogen upon setting, but this phenomenon can have negligible ill-effects if sufficient time after setting is allowed for this gas to be liberated. Compounds that are used in the vulcanization of some latex gloves can adversely affect the setting of this material, if these compounds come in contact with the impression either directly from the glove or indirectly via contact of the glove to the oral structures. However, thorough washing of these gloves with a detergent solution can rinse these potentially deleterious compounds away. The expense of this material has limited its use in orthodontics in the past; good handling characteristics before setting, low setting contraction, excellent dimensional stability after setting, and ability to form more than one model contribute to its attractiveness. Figure 12.2 shows an impression obtained with a polyvinylsiloxane impression material.

Polyether Rubber

A polyether oligomer with reactive-ring end groups will polymerize by a ring-opening reaction with an ester to form a cross-linked elastomer. A thorough mixing of the compo-



Fig. 12.2 An impression obtained with a polyvinylsiloxane impression material

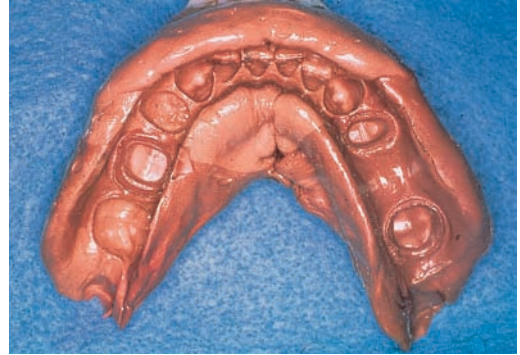


Fig. 12.3 An impression obtained with a polyether impression material

nents is required to avoid irritation of soft tissues by the ester. The hydrophilic nature of this material promotes dimensional instability unless the impression is kept dry. Its bitter

taste and high cost have limited the orthodontic use of this material. Figure 12.3 shows an impression obtained with a polyether impression material.

Properties of Impression Materials and Relationships to Clinical Use

Impression materials have many requirements for successful use in clinical dentistry and, since no current impression material completely satisfies all of these requirements, alternative materials are available for selection. Alginate impression material has been used extensively in orthodontics for obtaining study models. Its relative ease of manipulation, general acceptance by the patient, hydrophilicity, and cost-

effectiveness provide the major advantages. Its low tear strength, dimensional instability, and inability to be used for a second model are disadvantages. These disadvantages can be eliminated by the use of a hydrophilic polyvinylsiloxane, which has a higher cost than alginate impression material. A comparison of some of the properties of these two impression materials is provided in Table 12.4.

Table 12.4 Comparison of properties for alginate and polyvinylsiloxane impression materials

Property	Impression Material	
	Alginate	Polyvinylsiloxane
Working time (min)	1.25–4.5	1–4
Setting time (min)	1.5–5.0	3–6.5
Recovery from deformation (%)	98.2	99.5–99.95
Strain in compression (%)	8–15	1–6
Tear strength (g/cm)	380–700	1500–4300

From Craig, 1997

Properties Before Insertion into the Patient's Mouth

The clinical team is directly affected by the costs associated with the use of an impression material, since the overall cost in relation to effectiveness of the material usually dictates which material is selected. However, cost-effectiveness can be difficult to measure, since this effectiveness is dependent upon many separate factors. For example, if an impression must be retaken for any reason, then the extra material, the wasted chair-time, and the added patient discomfort must be considered in determining the cost-effectiveness of the material. Nevertheless, costs associated with obtaining and preparing the material for use can significantly affect the choice of material.

Material Cost and Shelf-Life

The material cost advantage of alginate hydrocolloid is superior to that of the other viscoelastic impression materials and is a significant factor in its high usage for orthodontic models. Although alginate impression material powder can be contaminated by water or excessive exposure to humidity, tightly closed containers promote long shelf-life of the powder. The greater cost of the synthetic elastomeric impression materials, especially the polyvinylsiloxane and polyether materials, and the greater susceptibility of their reactive ingredients to deterioration with time, diminish the attractiveness of these materials.

Ease of Preparation for Use

The tendency for the various sizes of powder particles for alginate material to distribute differently within a large container requires periodic remixing of the powder to avoid particle size separation. Failure to maintain an even distribution of powder particles will result in nonuniform mixes of the material. The susceptibility of the properties of alginate to the powder/water ratio used in the mix requires accurate measurement of these ingredients in order to maintain uniformity and optimum properties for clinical use. After these precautions are taken, alginate is easy to mix properly and, once mixed, has minimally sufficient

working time to be loaded into the tray and placed properly in the patient's mouth.

The mixing of a clinically useful synthetic elastomeric impression material involves the thorough mixing of two viscous components. Polyvinylsiloxane materials are often supplied with either passive mixing tips that attach to the ends of a dual-chamber syringe that dispenses the components in the optimum proportions, or with motor-driven mixing and dispensing systems. Such mixing systems tend to increase the effective cost of these materials, but can decrease the time required to prepare the material for use, with some recovery of this increased effective cost.

Properties While in the Patient's Mouth

An effective dental impression material must be viscous enough to be held in the impression tray while the tray is being inserted in the patient's mouth and must also conform to the unaltered shape of each of the oral tissues as found *in vivo*. Ideally this material would set on command into a perfectly elastic material without any harm or discomfort to the patient and without any dimensional inaccuracy.

Biocompatibility

With the exception of any unmixed ester in a polyether impression material, none of these impression materials has been associated with any significant adverse effects due to a lack of biocompatibility. Care must be taken to assure that any bite registration material is not excessively heated before being placed into a patient's mouth in order to avoid any thermal damage.

Patient Acceptance

Both taste and odor contribute to the acceptance by the patient when an impression material is placed over an entire arch. Although flavoring agents differ from manufacturer to manufacturer, the polysulfide and polyether materials are generally not well accepted. Additionally, the impression material must be sufficiently viscous that any excess material resists

flowing down the patient's throat. Polysulfide materials have been criticized for their tendency to flow too easily.

Flow (or Consistency)

In contrast to the lack of fluidity desired for patient comfort, the ideal impression material must quickly flow into the negative shape of the oral structures, while not distorting the shape of the soft tissues. The ability to use various consistencies of all of the synthetic elastomeric materials is a significant advantage of these materials. However, the prior handling of these materials can significantly affect their consistency, since the relative arrangements of the long molecules that are forming during the setting process are affected by the amount of shear induced in the material. A high shear rate associated with vigorous mixing or quick injection from a syringe causes the molecules to lie in a common direction, with a subsequent increase in fluidity and a decreased tendency to distort the shape of soft tissues. The arrangement of the molecules can rapidly change to become more intertwined and therefore more viscous, as the shear associated with mixing or injection decreases or ceases. The technique of fast placement of the impression material after mixing or rapid injection of the material onto the oral structures will promote its flow into the desired shape.

Wetting of Oral Structures

The ideal impression material would, upon placement in the patient's mouth, adapt quickly to the shape of the oral structures without incorporating air between the impression material and these structures. The contact angle (Chapter 1) of the freshly prepared impression material on each of the structures strongly influences the ease with which such air is entrapped. Ideally, no cleaning or treatment of the structures would be required, and the impression material would form a low contact angle, *i.e.*, would wet these structures as they are found *in vivo*, coated with a biofilm. However, since it is very difficult to maintain a natural biofilm on each of the oral structures while these contact angles are being measured, contact angles involving impression materials

are usually measured with water or artificial saliva as the fluid on the impression material. Such measurements indicate the relative degree with which the impression material will wet moist oral structures. These measurements show that, as setting continues, the contact angle of either artificial saliva or water on impression materials decreases, indicating improved wetting. Overall, hydrocolloid materials provide the greatest wetting, and condensation silicone materials provide the least wetting. Variations in wetting occur by brand for the polyvinylsiloxane materials, probably owing to variations in the molecular modification of the oligomers or the type or amount of surfactant.

Setting Dimensional Change

Ideally, an impression material would set with no dimensional change, provided it is used with the ideal model material, which also does not undergo change in dimensions on setting. Realistically, any change that increases molecular binding to form a more elastic material will be accompanied by an increase in density or a decrease in volume. The dimensional contraction associated with either alginate or polyvinylsiloxane is quite low, while that of the polysulfide and condensation silicone materials that undergo condensation polymerization during setting is significantly greater. Minimization of dimensional contraction is facilitated by minimization of the thickness of the impression material. Since any dimensional contraction of the material while setting is at least partially constrained by any adhesion to the impression tray, dimensional contraction translates easily into dimensional distortion, with different contractions in different directions. Gypsum model materials undergo linear expansion of approximately 0.3 % when setting, and this generally offsets the linear setting contraction of alginate and polyvinylsiloxane materials.

Setting Time

Ideally, an impression material would set as soon as it was properly formed against the oral structures. Alginate materials can be supplied as normal or fast-setting, with setting

times varying from two to five minutes from the start of mixing. The light-bodied synthetic elastomers generally require longer to set than the materials of the same type with different consistency, so these materials are generally mixed and placed first. The polysulfide materials generally require six minutes or longer to set, whereas the other synthetic elastomers require between three and six minutes to set.

Properties During Removal from the Patient's Mouth

Once set, the ideal impression could be removed easily with no patient discomfort, would withstand the process of being removed from a patient's mouth without tearing, and would recover exactly to the physical shape and dimensions it had prior to removal.

Flexibility

The flexibility of the set impression is a measure of the ease with which the material is elastically deformed and is inverse to the property of rigidity (or modulus of elasticity) defined in Chapter 1. Greater flexibility means that less force is required to elastically deform the impression in order for it to be removed from the undercuts that naturally occur in teeth. The ideal material would have very high flexibility, and its removal would go unnoticed by the patient. Polysulfide materials generally have the greatest flexibility after setting, followed by alginate, and then by the silicone and polyether materials.

Tear Strength

Given that available impression materials are not overly flexible, stresses are induced in the material as it is removed from the patient's mouth. If the impression material has low tear strength, these stresses can induce tearing of the impression. The ideal material would have a tear strength that exceeds the stresses induced by the removal process. Set alginate hydrocolloid has a tear strength that is about one-third to one-fourth that of the silicone and polyether materials and about one-tenth

that of some polysulfide materials. The low tear strength of alginate materials is one of their major deficiencies.

Creep Compliance

The ideal impression material would undergo no viscous deformation upon being removed from the mouth. However, available impression materials exhibit some creep after setting, as described in Chapter 1. It is important to note that the amount of viscous deformation that remains in an unloaded viscoelastic material is directly related to the time that it is maintained in the deformed condition. The optimization of dimensional accuracy is obtained by keeping the time of removal to a minimum.

Properties After Removal from the Patient's Mouth

Once removed from the patient's mouth, the ideal impression could be disinfected and then ignored completely, with no deleterious effects, while the clinician turns his or her attention to the needs of the patient. Eventually, the ideal impression could be used to make any number of accurate models.

Dimensional Stability

The ideal impression material would remain stable in its dimensions, regardless of the length of time between removal from the patient's mouth and its use to form the model, and regardless of its exposure to ambient conditions during this time. Additionally, the impression would remain stable throughout and after the model-forming process. A major deficiency of alginate hydrocolloid is its dimensional instability, and this instability is also found in the synthetic elastomeric materials that form by condensation reactions, *i.e.*, the polysulfide and the condensation silicone materials. Polyether, with its hydrophilicity, will take up water from a humid environment and exhibit some dimensional instability. The polyvinylsiloxane material, which gains at least some of its hydrophilicity from an added surfactant, can easily lose its hydrophilicity with the extraction of the surfactant from contact

with a humid environment; thus this material exhibits excellent dimensional stability.

In a similar fashion to the interaction of these impression materials with the humidity of the air environment, these materials also interact with gypsum as a gypsum model is formed in contact with the impression. Gypsum is known to incorporate any free additional water that is available at its surface during setting. Gypsum, as it sets, will extract the water from an alginate or a polysulfide impression material and may render the impression useless thereafter. The excellent dimensional stability of polyvinylsiloxane permits the pouring of a second accurate model.

Immunity to Disinfection

Although most hydrophobic impression materials may be disinfected by immersion in an appropriate solution, alginate and polyvinylsiloxane materials distort when immersed. Alginate material is known for its susceptibility to dimensional inaccuracy as it is exposed to various solutions, and there is often a conflict between exposure to sufficient disinfection solution to maintain proper infection control and exposure to too much solution to maintain dimensional accuracy. A current recommendation for disinfection involves spraying the

impression with disinfectant and isolating the impression in a sealed container. This procedure would also be appropriate for the other materials that exhibit less than excellent dimensional stability. Using disinfectant to replace pure water in the mixing of alginate material has also been evaluated to be effective and more efficient. Since the polyvinylsiloxane material demonstrates excellent dimensional stability, this material can be subjected to a more vigorous disinfection procedure with less concern for any deleterious effects.

Compatibility with Die Material

Gypsum is known also for its susceptibility to the retarding effects that gels have on its setting, and the gypsum surface formed against a hydrocolloid will never contain the detail found in the gypsum surface formed against a synthetic elastomer. Some ingredients are added to the alginate powder that will at least partially counteract this retardation, but the effectiveness of the gypsum accelerators that are found in the alginate are dependent upon the setting-time modifiers which are present in the gypsum powder. Therefore, some brands of gypsum are considered more compatible with certain brands of alginate.

Acknowledgment

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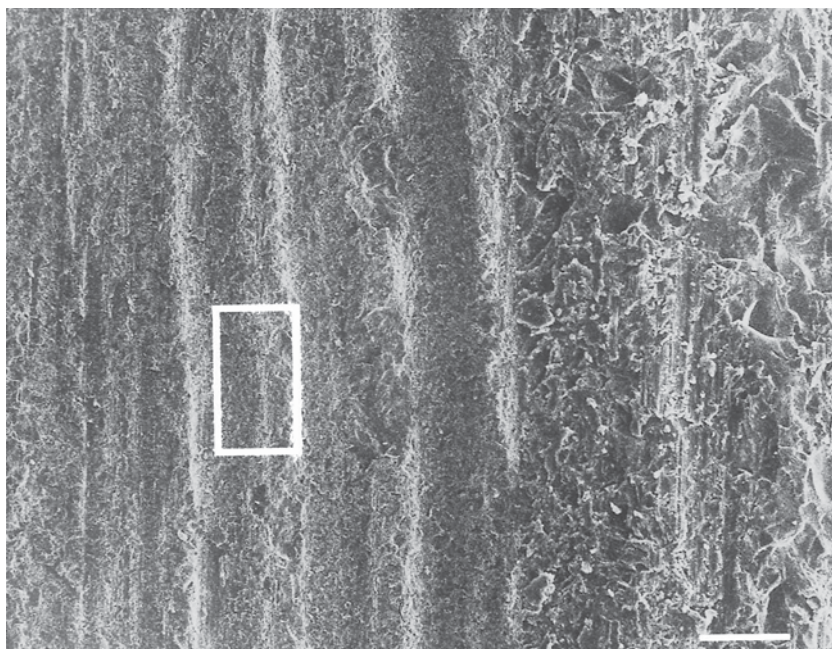
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13 Bonding to Non-Conventional Surfaces

Efstratios Papazoglou



Secondary electron image (SEM) of dental porcelain after grinding the glazed surface with a medium-roughness diamond bur, using a high-speed handpiece. Scale bar length = 10 μm . The right side of the photomicrograph is a magnification of the rectangular area on the left side

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Introduction

The scope of orthodontics has expanded over the past two decades to include more adult patients, and it is expected that many of these people will have restorations placed on their teeth. Although banding is always an alternative for the teeth that have restorations, bonding is desirable in aesthetic areas. Additionally, bands tend to accumulate more plaque than do brackets (Chapter 6).

The materials that are in use in restorative dentistry and prosthodontics include ceramics, casting alloys, resin composites, dental amalgams, and acrylic resins. The goal during ortho-

dontic treatment is that the appliances stay securely attached to their original position until the end of treatment. However, once treatment has been completed, the appliances should be easily removed without causing any permanent damage to tooth structure or permanent restorations. This chapter reviews the materials and techniques used for bonding to surfaces of restorative materials, termed *non-conventional surfaces* in contrast to the conventional bonding to tooth enamel discussed in Chapter 5.

Bonding to Ceramics

Ceramics are used in restorative dentistry as metal-ceramic restorations where the ceramic is bonded to a metal substrate or as all-ceramic restorations in the form of crowns and laminate veneers (Fig. 13.1). The majority of ceramic restorations are metal-ceramic crowns, where dental porcelain is manually formed in several layers (opaque porcelain, body or dentin porcelain, and a glaze) that are fired to a cast alloy substrate. The alloy is generally oxidized before firing of the opaque porcelain in order to achieve chemical bonding at the metal-ceramic interface, although the initial oxidation step is not required for at least one important commercial alloy. The composition of the dental porcelain corresponds to potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6 SiO_2$) or soda feldspar ($Na_2O \cdot Al_2O_3 \cdot 6 SiO_2$), or a combination of both, in a silica (SiO_2) network that contains leucite crystals ($K_2O \cdot Al_2O_3 \cdot 4 SiO_2$). During the firing cycles, the porcelain develops a principally vitreous (glass) silicate structure (Chapter 1). Several other ions are added as

oxides to the dental porcelain composition for control of color, opacity, sintering temperature, thermal contraction coefficient, and solubility. The microstructure of dental porcelain typically contains crystalline particles of leucite, opacifying oxides, and reinforcing oxides (principally alumina) in a glass matrix.

The all-ceramic restorations can be formed manually and then fired in a manner similar to dental porcelain, or cast in a manner similar to that for dental alloys. The all-ceramic restorations may or may not be core-reinforced with alumina, magnesia, or spinel. It will be very difficult for the orthodontist to determine the type and composition of a given all-ceramic restoration from clinical examination. What is important for the orthodontist is the external surface of the restoration; therefore, this chapter will focus on that aspect. The principal veneering material for all-ceramic restorations is leucite-containing feldspar. However, there are other ceramic materials that have been popular in the past, e.g., fluorine mica silicate in the

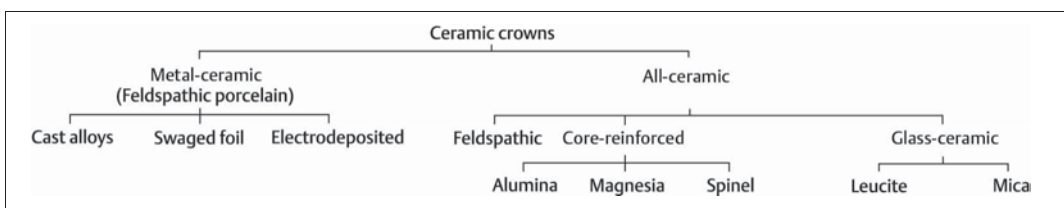


Fig. 13.1 General classification system for ceramic restorations

Dicor (Dentsply, York, PA, USA) castable all-ceramic system. What is important about these castable ceramic crowns is that all of their color is achieved from the external application of stains (metallic oxides). However, this system is not widely used in current dental practice. All other ceramic restorations achieve their color from the intrinsic color of the ceramic layers, with minimal application of external stains. The ceramic restorations should always

have a glazed or highly polished surface, as shown in Figure 13.2.

Acid etching with phosphoric acid in the fashion used for enamel bonding (Chapter 5) is ineffective for bonding orthodontic appliances to dental ceramic surfaces, since these ceramics are not attacked by this acid. Several alternative surface preparation techniques have been found to achieve satisfactory results: mechanical roughening with stones and dia-

Fig. 13.2 Secondary electron image of a glazed injectable feldspathic dental porcelain (OPC, Jeneric/Pentron, Wallingford, CT, USA) obtained with a scanning electron microscope (SEM). Scale bar length = 10 μm . (Porcelain disks for Figures 13.2 through 13.6 were provided by Dr. Isabelle Denry, College of Dentistry, The Ohio State University)

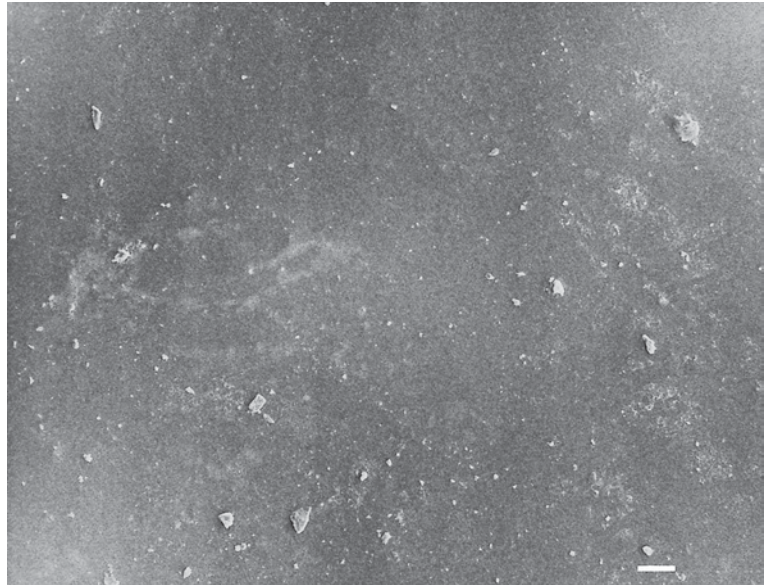
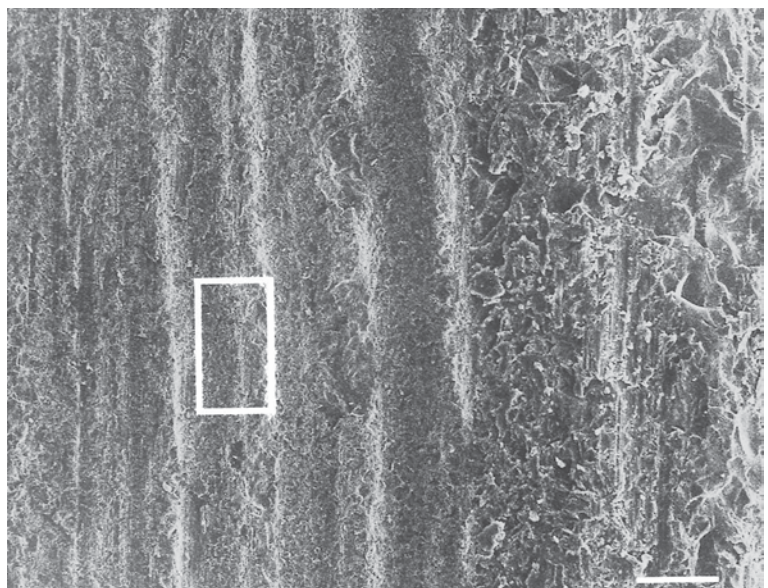


Fig. 13.3 Secondary electron image (SEM) of the same dental porcelain in Figure 13.2 after grinding the glazed surface with a medium-roughness diamond bur, using a high-speed handpiece. Scale bar length = 10 μm . The right side of the photomicrograph is a magnification of the rectangular area on the left side



monds (Fig. 13.3), sandblasting (Fig. 13.4), chemical roughening with hydrofluoric acid (Fig. 13.5), a combination of sandblasting and chemical roughening with hydrofluoric acid (Fig. 13.6), and chemical coupling with the use of silanes.

Roughening the porcelain surface with diamonds or stones (never with carbide burs) increases the bond strength, but does not provide sufficient retention for the whole period of

the orthodontic treatment. Additionally, such grinding may produce microcracks on the ceramic surface that might ultimately result in fracture of the restoration. Another technique that has been developed in the last few years is micro-etching of the ceramic surface. Small intraoral sandblasters with a contra-angle nozzle have been developed. These units have been approved by the United States Food and Drug Administration (FDA) for intraoral

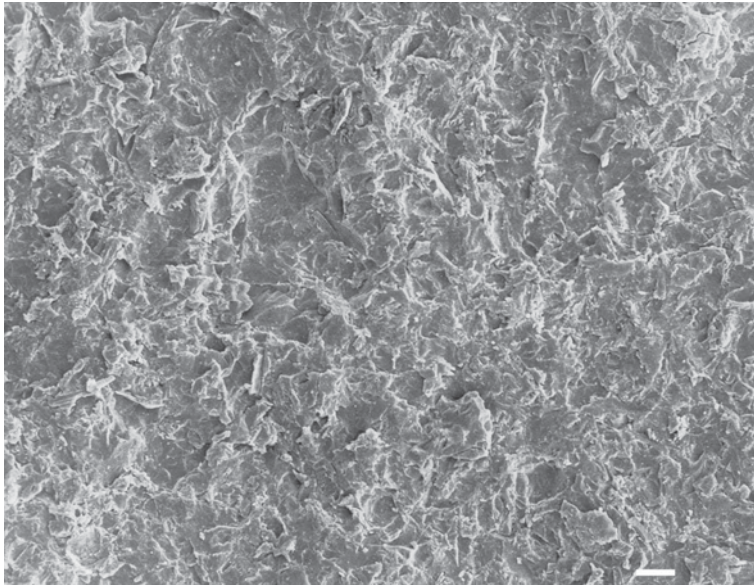


Fig. 13.4 Secondary electron image (SEM) of the feldspathic dental porcelain shown in Figure 13.2, after the glazed surface was sandblasted with a 50 µm alumina powder. Scale bar length = 10 µm

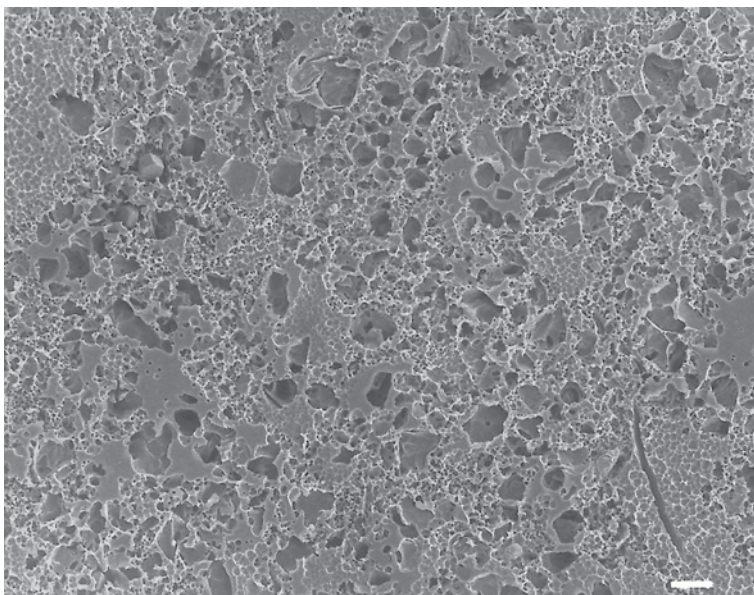
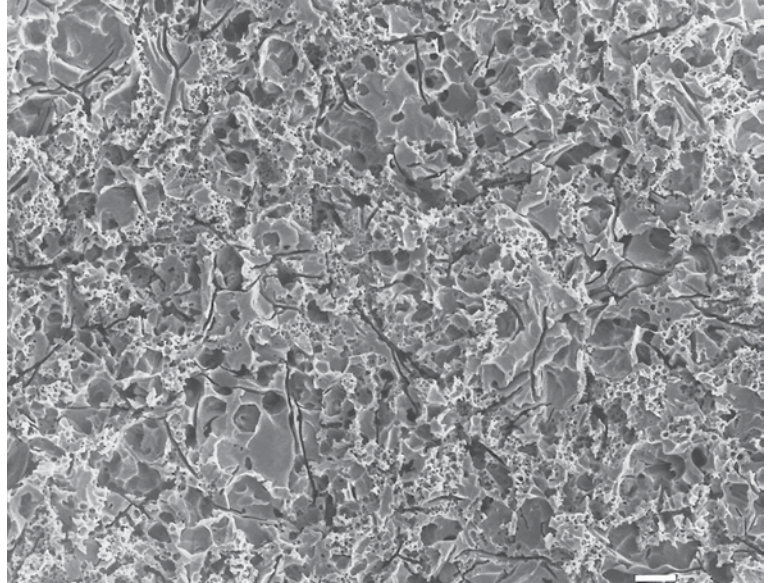


Fig. 13.5 Secondary electron image (SEM) of the same feldspathic dental porcelain shown in Figures 13.3 through 13.6, after the glazed surface was etched with a 9.6% hydrofluoric acid solution for 1 minute. Scale bar length = 10 µm

Fig. 13.6 Secondary electron image (SEM) of the same feldspathic dental porcelain shown in Figures 13.3 through 13.5, after the sandblasted surface was etched with a 9.6% hydrofluoric acid solution for 1 minute. Comparing this figure with Figure 13.5, it can be seen that etching after sandblasting results in a rougher surface than etching alone. Scale bar length = 10 μm



use. They use 50 μm or coarser aluminum oxide (Al_2O_3) powder connected to a compressed-air source in the operatory. An alternative powder that could be used in cases where patients have an allergic reaction to aluminum oxide is silicon carbide. It is best if micro-etching is accomplished with rubber dam isolation and with heavy-duty suction for collection of the ejected powder. The intraoral sandblasters can also be used for preparing the surfaces of other materials and for cleaning brackets before re-bonding.

Application of silane to the ceramic surface has been used to promote the adhesion of resin composites. For example, γ -methacryloxypropyltrimethoxysilane is a coupling agent (Chapter 9) that provides reactive sites for inorganic and organic components. This silane contains silanol groups that can bond with silanols on the ceramic surface, forming a siloxane (Si-O-Si) bond. Additionally, this silane contains methacrylate groups that can form covalent bonds with the polymer matrix of the resin composite. There are many different silane products on the market. Some consist of a single component, while others require mixture of two different components. It is very difficult to compare these products, since few have been evaluated in studies, and it is often difficult to compare the results of different studies.

Etching of the ceramic surface with hydrofluoric acid (HF) was introduced in the early 1980s for bonding porcelain laminate veneers. However, hydrofluoric acid is very potent, and requires considerable care in handling and isolation with a rubber dam. A commonly used hydrofluoric acid product has a concentration of 9.6% in gel form and is placed on the ceramic for two to four minutes (Figs. 13.5 and 13.6). Other available commercial products use 4% acidulated phosphate fluoride containing 1.43% hydrofluoric acid in gel form for two minutes. For areas of the ceramic surface where isolation is difficult, a 1.23% acidulated phosphate fluoride gel can be used for ten minutes. Acid etching of the ceramic surface is recommended when the maximum bond strength is required. When there is no such clinical requirement, micro-etching should be used, followed by conventional phosphoric acid to clean the surface and then placement of a silane coupling agent on the surface. Hydrofluoric acid etching without roughening of the ceramic surface does produce sufficient microporosity to achieve successful bonding in some cases.

Upon completion of orthodontic treatment, the ceramic surface should be restored as closely to the original condition as possible. Silicon carbide rubber points of sequential roughness levels and diamond polishing paste can be used to restore the original ceramic surface

finish. Many manufacturers provide porcelain polishing kits. However, use of the previously described techniques to increase the retention of orthodontic attachments may create irreversible damage to a ceramic restoration, especially when shade matching was achieved with external staining. The material that provided the original surface staining is removed during polishing, and shade matching with adjacent teeth is possible only with preparation of a new restoration. Additionally, if microcracks or other defects on the ceramic surface have been produced by the use of stones or during debonding, then more ceramic material will need to be removed to achieve a well-polished surface, thereby altering the original color and contours of the restoration.

The protocol for optimal bonding to ceramic surfaces is as follows. (1) The glaze is first removed by sandblasting, using $50\text{ }\mu\text{m}$ Al_2O_3 for two to four seconds. (2) The ceramic surface is then etched for two minutes, using 9.6% hydrofluoric acid in gel form. (3) Subsequently, two to three coatings of a silane coupling agent are applied to the etched surface, followed by drying. (4) Two layers of unfilled resin are then applied to form a thin coating. (5) Finally, the bracket is bonded to the prepared ceramic surface, using a highly filled Bis-GMA resin (Chapter 9). It is apparent that, in cases where

the color and integrity of the ceramic restorations are not to be disturbed, a risk of having to rebond the bracket during the course of orthodontic treatment should be assumed, and the above protocol should not be followed.

Published values for bond strength to porcelain are presented in Table 13.1. For these debonding experiments the load or force values (kg, lb, or N) that caused failure of the samples have been converted to strength values (MPa). Conversion of such load values to stress (load/area) values assumes a uniform stress distribution at the interface of the bracket and the tooth or other substrate surface. It has been proved that during the shear bond test the stress distribution at the interface is nonuniform. In addition, the results of shear bond testing have been found to depend upon the geometry of the bracket. The tensile test has a more homogeneous stress distribution at the interface and may be superior for evaluating the adhesive capabilities of resin composites under varying surface conditions. Finally, the torsion test may be more clinically relevant for measuring bond strength, since torsional forces are commonly used in orthodontics. Experimental results from different studies should be compared only for specimens of the same geometry and method of load application.

Bonding to Casting Alloys

Posterior teeth are often restored with full cast crowns. Although alloys for all-metal restorations were exclusively used for this purpose in the past, currently metal-ceramic alloys are often used for full cast crowns (Fig.13.7). In contrast to the alloys for all-metal restorations, metal-ceramic alloys contain oxidizable elements for promotion of porcelain adherence.

In 1984 the American Dental Association (ADA) classified casting alloys according to their noble metal content as *high noble*, *noble*, and *predominantly base metal*. The noble metals, from a dental materials perspective, are gold, platinum, palladium, ruthenium, iridium, rhodium, and osmium. While listed as a noble metal in chemistry textbooks, silver is not a noble metal in the oral environment because of its tendency to undergo corrosion. The

high-noble alloys contain a minimum of 40 wt% gold and 60 wt% noble metals; the noble alloys contain a minimum of 25 wt% noble metals; and the predominantly base metal alloys contain less than 25 wt% noble metals. In ADA specification no. 5, which was approved in 1988, there are four types of dental casting alloys. These alloys are classified according to their mechanical properties (tensile strength, hardness, and elongation): type I (soft), type II (medium), type III (hard) and type IV (extra hard). Crowns should only be fabricated from type III and type IV alloys. In the current version of this specification there is no longer a noble metal content requirement for the types I–IV casting alloys.

In the past, the most popular alloys for fabrication of all-metal crowns were the

Table 13.1 Shear bond strengths to porcelain

Material	Surface Treatment	Bonding Material	Debonding Time and Testing Environment	Bond Strength (MPa)	Reference
Porcelain, Ceramco dentin	Roughened (green stone) + silane bonding agent	Concise and Scotchprime	24 hr in H ₂ O	20.3 ^a	Kao <i>et al</i> (1988)
Porcelain, Ceramco dentin	Glazed + silane bonding agent	Concise and Scotchprime	24 hr in H ₂ O	13.9 ^a	Kao <i>et al</i> (1988)
Porcelain, Ceramco dentin	Roughened (green stone)	Concise	24 hr in H ₂ O	12.6 ^a	Kao <i>et al</i> (1988)
Porcelain, Ceramco dentin	Glazed	Concise	24 hr in H ₂ O	9.8 ^a	Kao <i>et al</i> (1988)
Porcelain, Vita dentin	Glazed + silane bonding agent	Concise	24 hr in H ₂ O, half thermocycled	11.1	Smith <i>et al</i> (1988)
Porcelain, Vita dentin	Roughened + silane bonding agent	Concise and Scotchprime	24 hr in H ₂ O, half thermocycled	8.1	Smith <i>et al</i> (1988)
Porcelain, Vita dentin	Roughened (240-grit SiC)	Concise	24 hr in H ₂ O, half thermocycled	2.1	Smith <i>et al</i> (1988)
Enamel	600-grit SiC and acid etch	Concise	24 hr in H ₂ O, half thermocycled	17.4	Smith <i>et al</i> (1988)

^aConverted to stress from original load values (lb).

high-noble gold alloys, which have outstanding corrosion resistance *in vivo*, good mechanical properties, and an aesthetically pleasing yellow color. Alternative alloys with reduced unit metal cost, satisfactory *in vivo* corrosion resistance, and mechanical properties similar to those for the high-gold alloys have been developed, including alloys with reduced gold content and silver-palladium alloys. Additionally, palladium-based, nickel-chromium and cobalt-chromium metal-ceramic alloys, as well as commercially pure (CP) titanium, have been used for all-metal restorations. Owing to the plethora of the available casting alloys, it is almost impossible for the orthodontist to clinically identify the type of alloy that has been used for a full cast crown, since the alternative alloys to the high-gold alloys generally have a white appearance. Most studies reported in the orthodontic literature have examined bonding to gold alloys.

Proper surface preparation and special adhesives are required for acceptable bonding to casting alloys. Although roughening the alloy surface with a stone increases the bond strength to brackets, intraoral sandblasters provide better results.

Research has shown that tin plating improves the bonding to noble alloys. During this procedure a thin layer of tin is electrolytically deposited on the alloy surface, improving the mechanical and chemical bonds to the resin composite. Another technique that yields satisfactory *in vitro* results is the electrolytic application of a gallium and tin solution (Adlloy) on the gold alloy surface. Although both of these techniques have appeared promising during laboratory testing, intraoral application is difficult. These techniques are not currently approved by the FDA for intraoral use, and there are no studies showing advantages for clinical orthodontic bonding.

In recent years, adhesives that chemically bond to metal surfaces have been developed. The commercial products Super-Bond C&B (Sun Medical, Kyoto, Japan) and C&B Meta-bond (Parkell, Farmingdale, NY, USA) combine 4-META (4-methacryloxyethyltrimethyl anhydride) with tributylborane monomer and a polymer powder. The same product without the powder is marketed for use as a liner with dental amalgams and has the commercial name of Amalgambond (Parkell); the Amalgambond Plus product from the same manufacturer contains the polymer powder. It is believed that 4-META forms a hydrogen bond with hydroxyl groups found on the prepared surface of the metal. *In vitro* studies have shown that brackets bonded to sandblasted gold alloys using these 4-META adhesives attain or exceed the bond strength values to acid-etched enamel. It has been found that these adhesives bond better to base metal alloys than to gold alloys.

The commercial products Panavia EX and Panavia 21 (J. Morita USA, Tustin, CA, USA) contain 10-MDP (10-methacryloyloxydecyl dihydrogenphosphate) and Bis-GMA, and these adhesives bond to metal surfaces by some presently unknown mechanism. Additionally, Panavia EX and Panavia 21 bond to dentin, enamel, and porcelain. Although there are no published studies on the bond strength values when these adhesives are used to bond brackets to metallic surfaces, their use is promising.

Intermediate resins have also been developed for the enhancement of bond strength values. The commercial products All-Bond 2 Primers A and B (Bisco, Itasca, IL, USA) have been shown to improve the *in vitro* bond strength to gold surfaces. Other materials that might be of interest are the glass-ionomer/Bis-GMA hybrid composites (Chapter 9). Clinical data for the performance of the new adhesives and intermediate resins are not currently available. Published bond strength values to gold alloys are presented in Table 13.2.

Bonding to Dental Amalgam

At present the majority of the commercially available dental amalgam products are the high-copper amalgams. Use of these products avoids the formation of the easily corroding γ_2 (Sn₈Hg) phase. The Ag-Sn-Cu powder particles that are mixed with mercury to form the dental amalgams are available in lathe-cut or spherical shapes, or as an admixture. The admixed dental amalgam products generally contain a mixture of powders of two different compositions; the particles can have the same shape or different shapes.

Posterior teeth often have buccal class V dental amalgam restorations. Bonding of brackets or tubes when there is ample amount of sound enamel surrounding the dental amalgam restoration is not difficult. However, when the

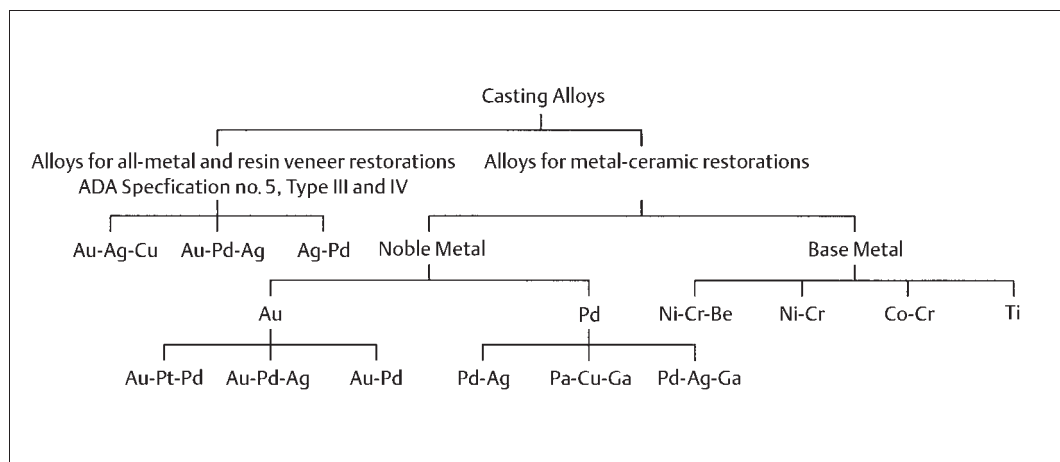


Fig. 13.7 General classification system for cast alloy restorations

Table 13.2 Bond strengths to gold alloy

Material	Surface Treatment	Bonding Material	Mode of Loading	Debonding Time and Testing Environment	Bond Strength (MPa)	Reference
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃) + tin plating	Superbond C&B	Tensile	24 hr in H ₂ O, half thermocycled	17.1	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃)	Superbond C&B	Tensile	24 hr in H ₂ O, half thermocycled	14.7	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃)	All Bond 2 A + B + Concise	Tensile	24 hr in H ₂ O	10.9	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Roughened (medium grit diamond)	Superbond C&B	Tensile	24 hr in H ₂ O, half thermocycled	8.9	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃)	All Bond 2 B + Concise	Tensile	24 hr in H ₂ O	7.6	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃) + tin plating	Concise	Tensile	24 hr in H ₂ O, half thermocycled	7.1	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Sandblasting (50 μ m Al ₂ O ₃)	Concise	Tensile	24 hr in H ₂ O, half thermocycled	4.8	Büyükyılmaz <i>et al</i> (1995)
45 % Au, 40 % Pd, 9 %In, 5 %Ag, 1 %Ga	Roughened (medium grit diamond)	Concise	Tensile	24 hr in H ₂ O, half thermocycled	2.9	Büyükyılmaz <i>et al</i> (1995)
Enamel (premolar bracket)	Acid etched	Concise	Tensile	24 hr in H ₂ O	16.6	Zachrisson <i>et al</i> (1993)
Enamel (lower incisor bracket)	Acid etched	Concise	Tensile	24 hr in H ₂ O	13.2	Zachrisson <i>et al</i> (1993)
Type IV gold alloy	Sandblasting (50 μ m Al ₂ O ₃), Adlloy	Concise	Shear	31 days in H ₂ O	6.86	Nollie <i>et al</i> (1997)
Type IV gold alloy	Sandblasting (50 μ m Al ₂ O ₃)	Concise	Shear	31 days in H ₂ O	3.36	Nollie <i>et al</i> (1997)
Enamel (premolar bracket)	Acid etched	Concise	Shear	31 days in H ₂ O	11.18	Nollie <i>et al</i> (1997)

size of the restoration is extensive, bonding to the dental amalgam surface is required. Higher bond strengths have been reported for bonding to spherical dental amalgam compared to lathe-cut or admixed amalgams. However, it is impossible for an orthodontist to clinically determine the specific type of dental amalgam that has been used by the restorative dentist. Sandblasting the surface of the restoration, followed by use of the previously discussed adhesives, 4-META, 10-MDP/Bis-GMA, and intermediate resins, improves bonding to dental amalgam. However, the bond strength achieved is at best about half that for resin composite to etched enamel. It should also be noted that sandblasting the dental amalgam surface (Figs.13.8 and 13.9) produces significantly better bonding than that achieved with a polished dental amalgam surface (Fig.13.10). This follows from the considerable difference in micromechanical retention offered by the two surface preparation conditions. However, when compared to roughening with a diamond bur (Fig.13.11 and 13.12), sandblasting of dental amalgam surfaces did not produce better bonding. Roughening with a stone bur (Figs.13.13 and 13.14) produces a surface topography on dental amalgam similar to that achieved with a diamond bur. (The overall relatively regular

patterns of the major surface architectural features in Figs.13.11 to 13.14 correspond to the relatively regular arrangements of the diamond and stone abrasive particles on the dental burs.) Published values of bond strength to amalgam surfaces are presented in Table 13.3.

Bonding to Resin Composites

Teeth often have resin composite restorations or resin composite laminate veneers on their facial surface in the area where brackets are to be bonded. (While both “*composite resin*” and “*resin composite*” are used in the dental literature, the latter terminology has been adopted in this chapter for consistency with Chapter9). As the resin composite restoration ages in the mouth, less unreacted methacrylate groups remain on the surface for cross-linking with the bonding resin. Additionally, the exposed filler particles are freed (“plucked out”) from the silane coupling agent. To achieve acceptable bonding to these restoration surfaces, the uppermost resin composite layer has to be removed with a diamond or carbide bur. Then the surface is acid-etched with 37% phosphoric acid. Silanation follows before ap-

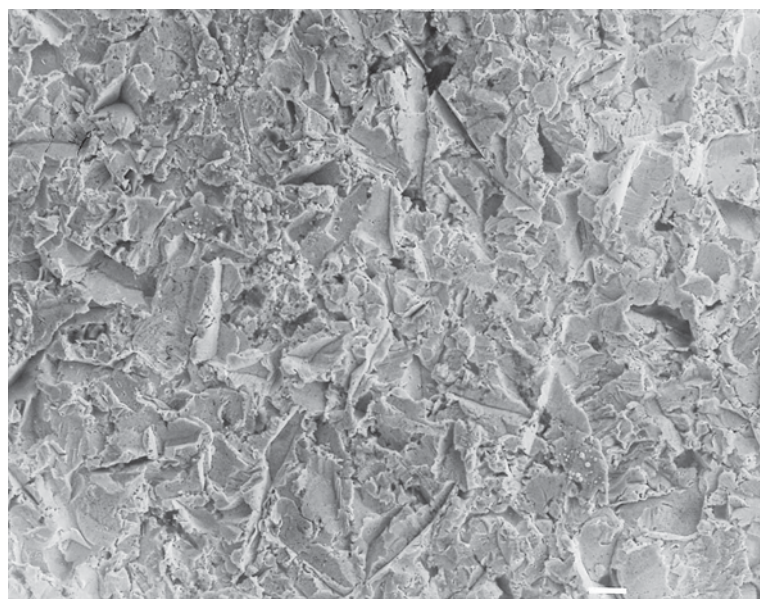


Fig. 13.8 Secondary electron image (SEM) of a high-copper admixed dental amalgam (Dispersalloy, Dentsply Caulk, Milford, DE, USA) sandblasted with 50 μm alumina powder. Scale bar length = 10 μm . (The dental amalgam samples for Figures 13.8 through 13.14 were provided by Dr. Peter Monaghan, College of Dentistry, The Ohio State University)

Fig. 13.9 Secondary electron image (SEM) of a high-copper spherical dental amalgam (Tytin, Kerr/Sybron Dental Specialties, Romulus, MI, USA) sand-blasted with a 50 μm alumina powder. Scale bar length = 10 μm . The similar appearances of this figure and Figure 13.8 suggest that the surface topography is controlled by the abrasive particles used for sand-blasting. However, the smaller scale of the surface architecture in both figures, compared with the nominal 50 μm abrasive particle size, may indicate some role of the two dental amalgam microstructures

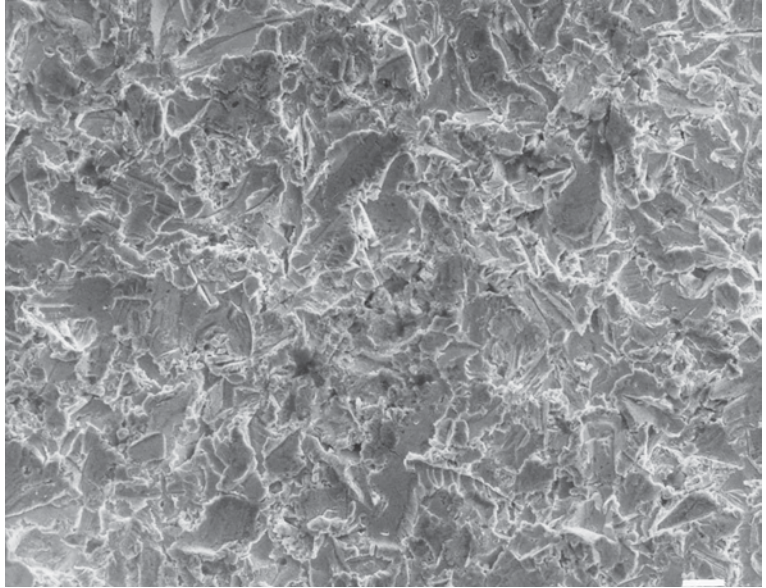
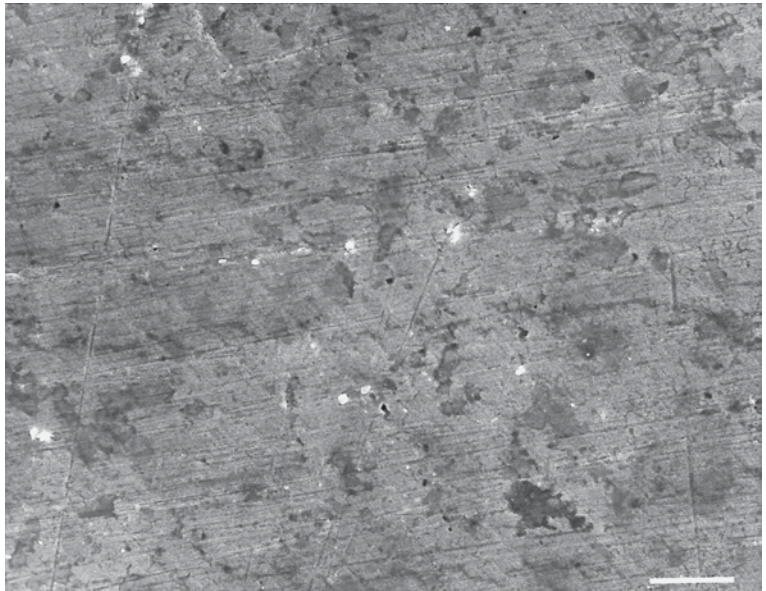


Fig. 13.10 Secondary electron image (SEM) of a polished conventional low-copper lathe-cut dental amalgam (Garfield's Alloy, Garfield Refining Co., Chicago, IL, USA). Scale bar length = 10 μm



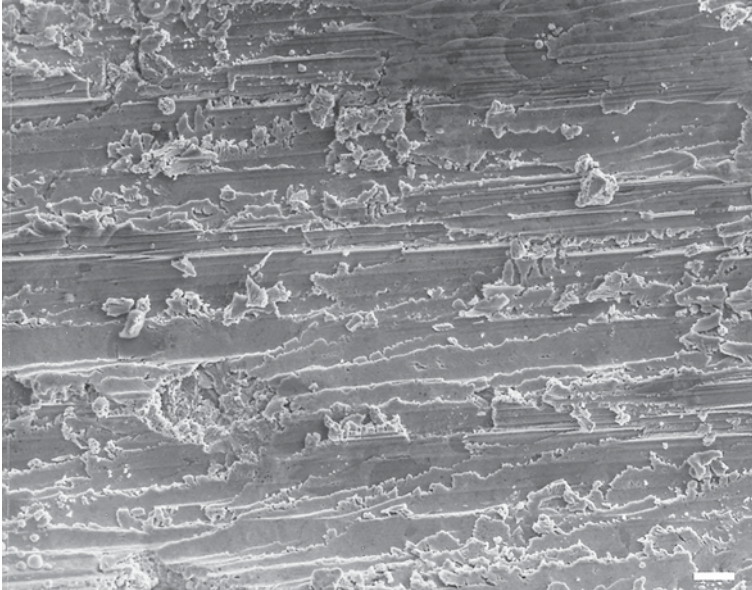


Fig. 13.11 Secondary electron image (SEM) of a high-copper admixed dental amalgam (Dispersalloy) abraded with a medium-roughness diamond bur. Scale bar length = 10 μm

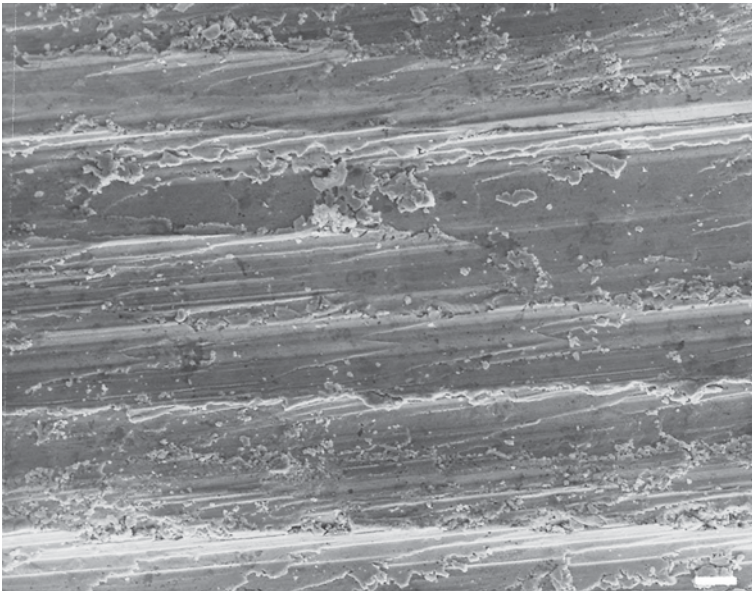


Fig. 13.12 Secondary electron image of a conventional low-copper lathe-cut dental amalgam (Garfield's Alloy) abraded with a medium-roughness diamond bur. Scale bar length = 10 μm . Comparison of this figure and Figure 13.11 suggests that the major topographical features are controlled by the abrasive particle arrangements on the diamond burs, but there may be some contribution from the differences in the microstructures of the two dental amalgams

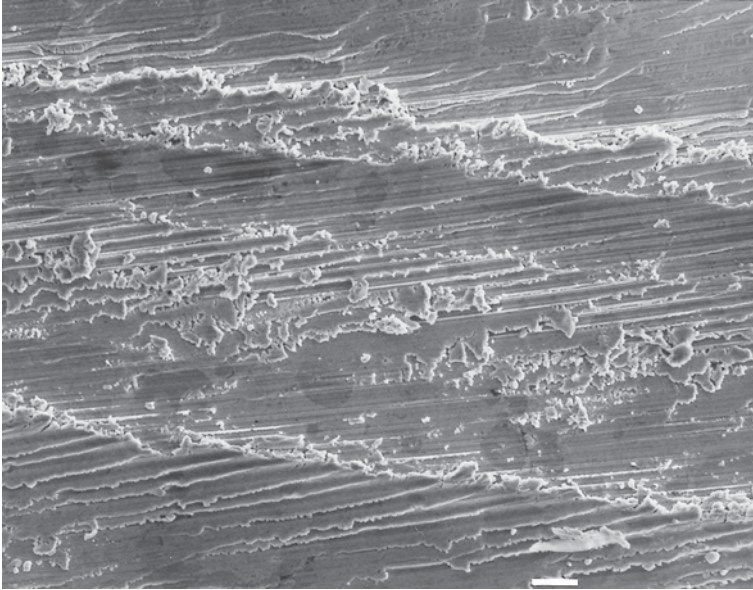


Fig. 13.13 Secondary electron image of high-copper admixed dental amalgam (Dispersalloy) abraded with a green stone bur. Scale bar length = 10 μm

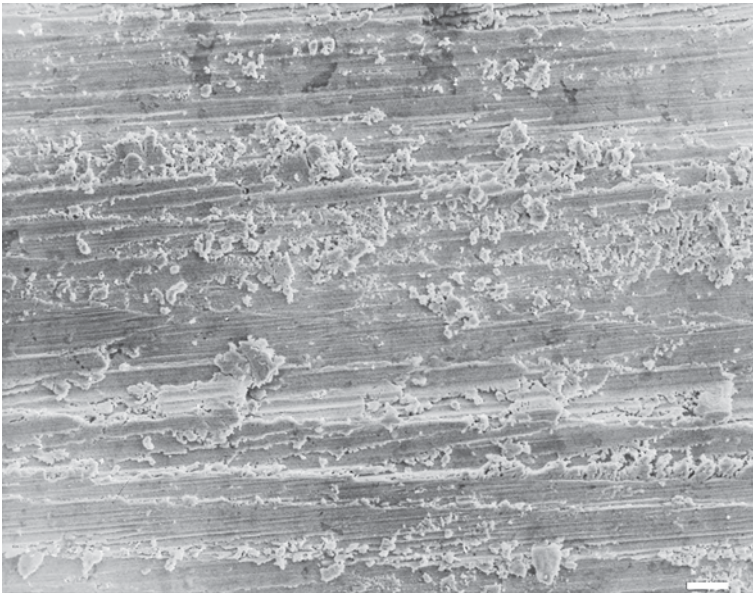


Fig. 13.14 Secondary electron image of conventional low-copper lathe-cut dental amalgam (Garfield's Alloy) abraded with a green stone bur. Scale bar length = 10 μm . Comparison of this figure and Figure 13.13 suggests that the major topographical features are controlled by the stone abrasive particle arrangements on the burs, but there may be some contribution from the differences in the microstructures of the dental amalgams

Table 13.3 Bond strengths to dental amalgam

Material	Surface Treatment	Bonding Material	Mode of Loading	Debonding Time and Testing Environment	Bond Strength (MPa)	Reference
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	Superbond C&B	Tensile	24 hr in H_2O	6.4	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	All-Bond 2 Primers A + B, Concise	Tensile	24 hr in H_2O	6.3	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	Geristore	Tensile	24 hr in H_2O	5.5	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Rough (medium grit diamond)	All-Bond 2 Primers A + B, Concise	Tensile	24 hr in H_2O	5.3	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	Concise	Tensile	24 hr in H_2O	5.0	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	Panavia Ex	Tensile	24 hr in H_2O	4.5	Zachrisson <i>et al</i> (1995)
Lathe-cut non- γ_2 , ANA 2000	Sandblasting (50 μm Al_2O_3)	Scotchbond MP, Concise	Tensile	24 hr in H_2O	3.4	Zachrisson <i>et al</i> (1995)
Enamel (premolar bracket)	Acid etched	Concise	Tensile	24 hr in H_2O	16.6	Zachrisson <i>et al</i> (1993)
Enamel (lower incisor bracket)	Acid etched	Concise	Tensile	24 hr in H_2O	13.2	Zachrisson <i>et al</i> (1993)
Admixed, Dispersalloy	Sandblasting (50 μm Al_2O_3), Adlloy	C & B Metabond	Shear	10 wk in H_2O	13.19	Gross <i>et al</i> (1997)
Admixed, Dispersalloy	Sandblasting (50 μm Al_2O_3)	C & B Metabond	Shear	10 wk in H_2O	8.43	Gross <i>et al</i> (1997)
Admixed, Dispersalloy	Sandblasting (50 μm Al_2O_3)	Concise	Shear	10 wk in H_2O	4.53	Gross <i>et al</i> (1997)
Admixed, Dispersalloy	Sandblasting (50 μm Al_2O_3), Adlloy	Concise	Shear	10 wk in H_2O	4.15	Gross <i>et al</i> (1997)

plication of an unfilled resin and bonding. The reported bond strengths to resin laminates are about 60–85% of the bond strengths to etched enamel, and this level of bond strength has

been judged adequate to provide clinically acceptable retention. Use of more potent etching agents like hydrofluoric acid has not been tried.

Bonding to Acrylic Resins

In highly traumatic circumstances teeth can become fractured at or below the bone level. If the remaining root is sufficiently long and judged adequate to support a restoration, there is a need to extrude it orthodontically after endodontic therapy. When such a fractured tooth is located in a region of the mouth where aesthetics are important to the patient, there is a need for placement of a provisional restoration prepared from poly(methyl methacrylate) (PMMA) resin or resin composite. If a resin composite has been used for

the provisional restoration, the protocol described above for bonding to resin composites is followed. However, if PMMA has been used, the surface of the provisional restoration has to be first wetted with methyl methacrylate for three minutes. The brackets can then be bonded using a bonding agent (*e.g.*, unfilled resin) and resin composite. Alternatively, the bracket can be attached using PMMA with the brush-bead technique, or it can be embedded in the PMMA provisional restoration.

Implant Attachments

Dental implants are increasingly being used in situations where there is insufficient orthodontic anchorage from the natural teeth. Orthodontic appliances may be bonded to screw-retained implant-supported restorations, which may be all-metal restorations or restorations veneered with porcelain, resin composite, or

acrylic resin. The techniques for bonding brackets to such surfaces are identical to those previously described. In posterior areas of the mouth where aesthetics are not important to the patient, brackets or tubes can be soldered extraorally to screw-retained crowns or abutments using a low-fusing silver solder.

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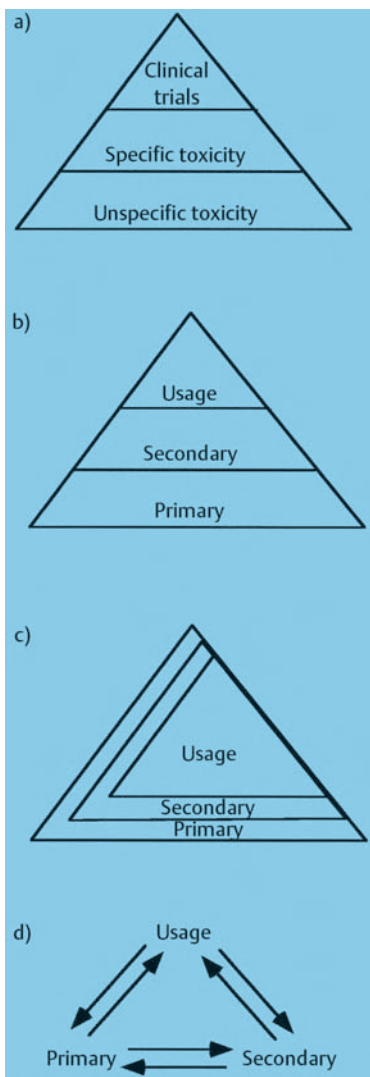
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14 Principles of Biocompatibility

John C. Wataha



Schemes for testing biocompatibility.

(a) The oldest scheme used “unspecific” toxicity tests first, followed by “specific” toxicity tests, and then by clinical trials. Only materials that passed one level were tested further. Unspecific tests were those that were not directly relevant to the use of the material. (b) This scheme employs primary, secondary, and usage tests, and it is still commonly employed today. The scheme differs from (a), because it emphasizes many cellular reactions in addition to toxicity. As in (a), each level of the test screens for the tests above it. Primary tests measure basic biological properties such as toxicity or mutagenicity of the material. Secondary tests assess more advanced properties such as allergenicity. Usage tests are equivalent to clinical trials. (c and d) Newer schemes for biocompatibility testing that recognize the need to use several types of tests together and that the evaluation of biocompatibility of a material is an ongoing process

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Introduction: Relevance of Biocompatibility to Dentists

Biocompatibility is a complex and rapidly evolving research area that may seem beyond the purview of practicing dentists. However, biocompatibility issues should be of concern to every practitioner because these issues have profound ethical, social, technical, and legal implications for dental practice. The practitioner's potential concerns about biocompatibility can be organized into four areas: safety issues for the patient, safety issues for the dental team, compliance issues, and liability.

Safety of the Patient

Clearly, one of the primary concerns of any dental practitioner is to avoid harming the patient. This concern is especially important in orthodontic practices where many patients are children or young adults. Throughout the years there is evidence that, while adverse reactions to dental materials are not common, they can occur for many types of materials used in orthodontics, including alloys, resins, and cements. A national registry in Norway, where there are 4.3 million people and 3800 dentists, reported 674 adverse reactions from 1993 to 1997. These adverse events involved all classes of dental materials and occurred locally and systemically. A relatively rare frequency of problems (1:2600) has been reported for dental casting alloys, including the nickel-based alloys used in orthodontics. Yet most researchers agree that, because many adverse reactions may be unreported, existing reports may not be accurate, and that better documentation of the extent of these reactions is needed.

Two biocompatibility-patient safety issues have been prominent in orthodontics in recent years. The first is the hypersensitivity of the patient to dental biomaterials. Classically, this concern has focused on nickel allergy. The incidence of nickel allergy in the general population is somewhere between 10% and 20%, being far more common in females than males. The frequency with which nickel elicits adverse responses in sensitive patients through oral exposure is controversial, but rarely can be spectacular. Chapter 15 deals with these issues in depth. There is also growing concern about hypersensitivity of the patient to latex and

other resin-based materials. Although not common, patients can suffer severe or even fatal allergic reactions to these materials. There have been reports of a growing incidence of contact sensitivity to a variety of substances, including dental materials, in children. One such report found that 49% of children had sensitivity to some type of material or food. Since orthodontists treat many children, these types of reports deserve scrutiny.

The second major biocompatibility issue that has faced orthodontists in recent years is the question of the estrogenicity of dental resins, particularly those containing the chemical bisphenol A, one of the two components that react to form Bis-GMA (Chapter 9). Estrogenicity is the ability of chemicals from the environment, called xenoestrogens, to mimic the hormone estrogen in the body of the exposed person. Because natural estrogens have many powerful and widespread effects on growth and development, xenoestrogens are a concern for all animal life in our environment. A single article published in 1996 claimed that dental sealants released sufficient amounts of the xenoestrogen bisphenol A to be a plausible threat to children. Although unsubstantiated by other reports, these issues are alarming to dental patients and capture significant coverage in the media. The issue of bisphenol A in dentistry is covered more extensively at the end of this chapter.

Thus, there is evidence that the biomaterials used by dental practitioners can pose some risk to patients. It is the practitioner's problem to decide whether this evidence has merit and to assess the risks of these issues in his or her own practice.

Safety of the Dental Team

The area of biocompatibility of materials is also relevant to the practitioner from the standpoint of the health of the dental team. In many cases, the risk of adverse effects of biomaterials is much higher for the dental team than for the patient because of the chronic exposure of the dental team and the manipulation of materials when they are being placed, setting, or being removed. The classic example of this

problem is with dental amalgam, since the release of mercury vapor from amalgam during placement or removal is substantially higher than after it has set in the cavity preparation. However, these types of issues are also relevant to the orthodontist.

The primary risk for the dental team in orthodontics appears to be contact with latex-based and resin-based materials. These adverse effects can be from cumulative irritation or from allergenic responses. Ironically, not only do gloves not protect against contact with some of these materials (which are capable of moving through gloves), but the gloves themselves are a source of the problem. One study in Sweden reported that 15% of dentists (vs. 9% in the general population) had itching on the hands in response to gloves, particularly latex gloves. The mechanisms by which these materials cause problems are not known, but there is evidence that some resin components such as HEMA (hydroxyethyl methacrylate), TEGDMA (triethylene glycol dimethacrylate) and camphoroquinone (Chapter 9) are capable of activating immune cells directly. In any case, the reactions to many types of dental materials can be severe, career-threatening, and even life-threatening in rare cases to dental practitioners and auxiliaries. It is therefore in the best interest of the practitioner to understand dental biocompatibility issues.

Compliance with Regulatory Issues

Practitioners are affected by biocompatibility issues because these issues are closely linked to regulatory issues that govern dental practice. An example of this link is with dental amalgam. Because of the biological concerns about mercury, regulators have considered monitoring and restricting the amount of mercury in wastewater from dental practices. This debate has spurred considerable research in methods to eliminate particulate and elemental mercury from dental waste. Most dental practitioners in the United States are keenly aware of the many regulations imposed by the Occupational

Health and Safety Administration (OSHA) of the federal government on dental practice. These regulations are, for the most part, designed to minimize risks to dental personnel from agents in dental restorative materials and devices. Thus, biocompatibility concerns directly influence regulatory policy.

One current regulatory issue with its origins in biocompatibility is hypersensitivity to latex. Latex rubber and its associated proteins are capable of causing severe and sometimes life-threatening allergic reactions in patients. Although the severest reactions are apparently rare, their occurrence has fostered formation of groups opposed to the use of latex in health care. In turn, several U.S. state legislatures have debated but not passed bans on latex gloves in dental and medical practice. As reactions to latex products become more common and better documented, such regulatory pressures are certain to persist.

Liability

Biocompatibility issues also influence liability issues, which affect dental practitioners. Because dental materials can affect the well-being of patients or dental auxiliaries, the practitioner assumes a legal risk when using these materials. The frequency of litigation as a result of biomaterials causing harm to patients is unclear but is probably low. Nevertheless, when these problems occur, they are at best emotionally and financially stressful, and at worst devastating to the practitioner. The litigious potential of these issues is enhanced by the facts that orthodontic practices treat many children and that many staff are women of child-bearing age. Examples of such issues in orthodontics include loss of enamel from enamel-bracket debonding, systemic allergy to nickel-containing orthodontic wires or appliances, or development in a staff member of a disabling hypersensitivity to an orthodontic resin material. Thus, biocompatibility issues are important to the orthodontic practitioner from a legal standpoint.

Definition of Biocompatibility: Concepts and Misconceptions

Accepted Definition and Key Points

Given the importance of biocompatibility issues to dental practitioners, it is surprising how few understand what biocompatibility really is and what its consequences are. One widely accepted definition of biocompatibility is “the ability of a material to elicit an appropriate biological response in a given application.” If examined closely, this definition implies an interaction between a host, a material, and an expected function of the material (Fig.14.1). All three factors must be considered and be in harmony before the material can be considered biocompatible. A discussion of several key points will reinforce this idea.

The first key point to understand about biocompatibility is that there are no truly *inert* biomaterials. When a material is placed into living tissue, interactions with the complex biological systems around it will occur, and those interactions will result in some sort of biological response. The interactions that occur will depend upon the material, the host, and what forces and conditions are imposed on the material (its function). Regardless, the material will affect the host, and the host will affect the material. The term “inert” applied to a biomaterial implies an absence of such interactions. Most scientists agree today that no material is truly *inert* in the body.

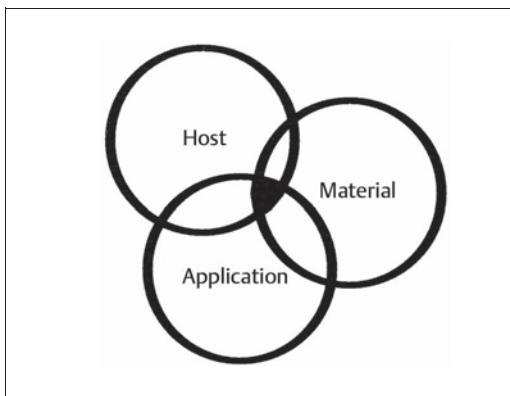


Fig. 14.1 Diagram illustrating the interactions between host, material, and clinical application of the material that are important in biocompatibility

A second key point about the definition of biocompatibility is that it is a dynamic, ongoing process, not a static one. If one has a dental implant that is fully osseointegrated into bone today, does that mean that it will remain osseointegrated over time? The response of the body to a material can change over time (*i.e.*, it is dynamic), because the body may change through disease or aging; the material may change through corrosion or fatigue, or the loads placed on the material may change through changes in the occlusion. Any of these changes may alter the conditions that initially promoted an appropriate and desired biological response. The interactions between material, host, and function continue over time; therefore, the biological response to a material is a dynamic, ongoing process.

A third key point about the definition of biocompatibility is that it is not a property only of a material, but of a material interacting with its environment. Consider an example with dental and orthopedic implants. A properly placed CP (commercially pure) titanium implant or a plasma-sprayed hydroxyapatite-coated (HA-coated) Ti-6Al-4V implant will osseointegrate with mandibular bone over time. According to currently accepted guidelines, this means that the interface with bone will be located within approximately 10 nm of the implant, without intervening fibrous tissue. If a cobalt-chromium alloy is placed in the same dental implant situation – same host, same placement technique, same load – no osseointegration will occur. Conversely, when Ti-6Al-4V is used as an orthopedic implant alloy for hip arthroplasty, the femoral head (ball) portion of the implant causes wear of the acetabulum (socket), which is typically fabricated from ultrahigh-molecular-weight polyethylene (UHMWPE). The small particles of UHMWPE cause irritation locally and at remote sites because of movement of the debris with circulation of the blood; ultimately failure of the implant occurs. Yet the much harder cobalt-chromium alloy will do well in this orthopedic application. Acetabular cups fabricated from zirconia have been used with the Ti-6Al-4V alloy (which may be HA-coated for more rapid osseointegration), but the zirco-

nia sockets have much greater weight and cause wear of the titanium alloy. Thus, it is not always appropriate to label the Ti-6Al-4V alloy as “biocompatible” and the cobalt-chromium alloy as “incompatible” because this classification depends upon the interaction of the material with its environment. One cannot define the biocompatibility of a material without defining the location and function of the material. In this sense, biocompatibility is like color (Fig. 14.2). We often ascribe color to a material, but color is a property not only of the material but also of the interaction of the material with light. Without the light interaction there is no color. The color of the material depends upon the light source, how the light interacts with the material, and the visual response of the observer.

Relevance to Dental and Orthodontic Practitioners

The complexities mentioned in the previous paragraphs may leave the practitioner wondering about the relevance of the definition of biocompatibility to dental practice. Yet there are profound consequences of this definition for orthodontic practitioners. For example, the practitioner must always consider the health and habits of the patient when assessing the biological response to materials. Is the patient diabetic? Does the patient smoke? If so, the

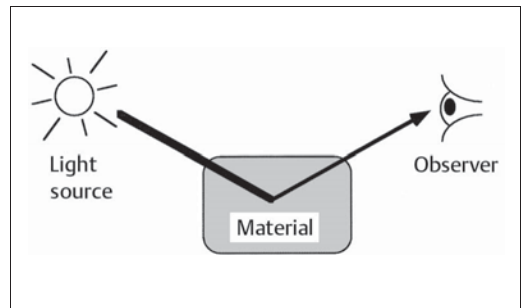


Fig. 14.2 The color of a material depends upon the interaction of the material with light and the observer's interpretation of the affected light. Thus, color is a property of a material interacting with its environment. Biocompatibility is also a property of a material interacting with its environment

response of the gingivae to metallic bands may be different. Does the patient ingest many acidic drinks? The corrosion properties of the archwires may be different (Chapter 4). The practitioner must consider the particular clinical application and patient, and not assume that, because a certain alloy is biologically acceptable as an archwire, it will be acceptable as a bracket or a band or a spring. Resin materials that are biologically acceptable as removable appliances may or may not be acceptable as resin-based cements. Finally, the practitioner must monitor the patient over time. A patient who is not allergic to nickel today might become allergic in the future.

Measurement of Biocompatibility

Although materials have been used in the body for thousands of years, only recently have the public and various governmental agencies required some assurance that such materials are safe and effective. These regulatory pressures have resulted from many sources, including the movement toward the ethical treatment of patients, an increased awareness of patients about the risks involved in health care, and concerns of health practitioners about litigation by patients. Unfortunately, assessment of the biocompatibility of a material is a complicated matter that involves several sophisticated types of biological tests, tests of physical properties such as corrosion, and risk-benefit analysis.

The complexity in assessing the biocompatibility of materials is often bewildering and frustrating to the practitioner and the public. However, in spite of its complexity, biocompatibility testing of dental materials is the only means currently available to try to assure the safety of the patient and dental team.

Types of Biocompatibility Tests

Biocompatibility is measured using three types of biological tests: *in vitro* tests, animal tests, and usage tests. Each of these tests is described in detail in the following paragraphs. Although

it is unlikely that the practicing orthodontist will need to evaluate results of these tests directly, it is important that he or she understands how materials are approved for use, since ultimately it is the practitioner who must assume the direct legal risks of using materials in the patient. The following paragraphs describe the advantages and disadvantages of each type of biological test, so that the practitioner will have a foundation for understanding the issues that often surround the biocompatibility of materials (Table 14.1).

In vitro biocompatibility tests are performed in a test tube, cell-culture dish, or otherwise outside of a living organism. These tests are quite diverse, but generally place cells or bacteria in contact with a material. For example, a strain of bacteria may be used to assess the ability of a material to cause mutations (the so-called Ames test) or a strain of fibroblasts may be grown on a culture plate and exposed to liquid extracts from a material. The effect of the material is generally determined by measuring the number, growth rate, metabolic

function, or other cellular function of the cells exposed to the materials. The *in vitro* test has the advantages of being controllable experimentally, repeatable, fast, relatively inexpensive, and relatively simple. In addition, these tests generally avoid the ethical and legal issues that surround the use of animals and humans. However, the primary disadvantage of *in vitro* tests is their questionable relevance to the use of the material in the mouth. Because these tests are done outside of an intact organism, the many complex interactions that comprise the biological response in the body are not present. Consequently, the results of *in vitro* tests may be misleading as to the ultimate biological response of the material.

Animal tests for biocompatibility are different from *in vitro* tests, because the material is placed into an animal, usually a mammal. For example, the material may be implanted below the skin of a mouse, or placed into the tooth of a rat, dog, cat, sheep, goat, monkey, or other animal. By using a mammalian organism, this type of test allows the many complex interactions

Table 14.1 Advantages and disadvantages of types of biocompatibility tests

Type of Test	Advantages	Disadvantages
<i>In vitro</i> tests (cell cultures)	Experimentally controllable Relatively fast Relatively inexpensive Avoid use of human subjects Avoid use of animals (sometimes) Avoid ethical issues	Questionable relevance if structured incorrectly
<i>In vivo</i> tests (animals)	Intact organism – measure complete biological response Can measure responses that are not possible to observe <i>in vitro</i> Avoid use of human subjects Avoid some ethical issues	Time-consuming Expensive Can be difficult to control experimentally Can be difficult to interpret experimentally Ethical issues - animal use
Usage tests (clinical trials)	Relevant Measure complete biological response	Difficult to control experimentally Time-consuming Expensive Ethical issues – humans Legal issues – humans Can be difficult to interpret experimentally

between the biological environment and the material to occur. Thus, the biological response is more comprehensive and relevant than with the *in vitro* test. However, it is often difficult to control variables in these tests. For example, the chewing habits of a rat may alter the material in ways that are not relevant to humans. Furthermore, it is often difficult to quantitatively assess the biological response because it is so complex. Ethical concerns and animal welfare issues are increasingly important in these types of tests. Moreover, these tests are time-consuming and expensive. Finally, and most important to the practitioner, the question of relevance remains, because there are always

questions about the appropriateness of using an animal species to represent the human response.

Usage tests are essentially clinical trials of the material. In these tests, the material is placed into a human volunteer in its final intended manner. The usage test is, by definition, the most relevant biocompatibility test, and all other tests must be measured against it for relevance. However, usage tests have many complications and problems. They are expensive, time-consuming, extraordinarily difficult to control, difficult to interpret, and may be legally and ethically complex.

Correlation Among Types of Tests

Several studies have shown the problems of correlation among *in vitro*, animal, and usage tests for biocompatibility. A classic example occurs with zinc oxide-eugenol cements. Clinical experience and clinical trials have shown conclusively that this cement has virtually no adverse pulpal effects, yet tests in animals (implanted subcutaneously) showed significant inflammation, and *in vitro* cell-culture tests showed that this cement was severely toxic. Discrepancies such as these led many researchers to question the usefulness of any test except the usage test to evaluate dental biomaterials. Today, most researchers recognize that *in vitro* and animal tests play important roles in the biological evaluation of dental materials. However, it is also recognized that the structure of any biocompatibility test is absolutely critical to its relevance. If meaningful data are to be ob-

tained from biocompatibility tests, then close scrutiny of the test procedure is essential to assure that the testing conditions are as relevant as possible. For example, since the clinical use of zinc oxide-eugenol cement is such that a dentin barrier remains between the cement and the pulp, subcutaneous implantation and cell-culture tests that do not replicate this relationship give misleading results. Studies that have interposed a dentin barrier between the tissues or cells and the cements give correlations with clinical results that are much more favorable. For *in vitro* tests, the type of cells used, the conditions of exposure, and the type of response measured are critical. For animal tests, the animal system, the site of implantation of the material, and the duration of the test are all important features.

Using Different Tests Together

For about twenty years, researchers have recognized that the most efficient, cost-effective, and relevant way to evaluate the biocompatibility of materials is by employing a combination of *in vitro*, animal, and usage tests. However, the ways in which these tests are used together and the philosophies about the roles of each type of test have changed somewhat over the years. Early researchers proposed a pyramid scheme

of “unspecific toxicity, specific toxicity, and clinical trials,” as shown in Figure 14.3a. Unspecific tests were those in which the conditions of the test did not necessarily reflect those of the material's use. Specific toxicity tests were those where the conditions of the testing were more relevant to the clinical use of the material. About ten years later, others proposed a pyramid scheme of similar philosophy, divided

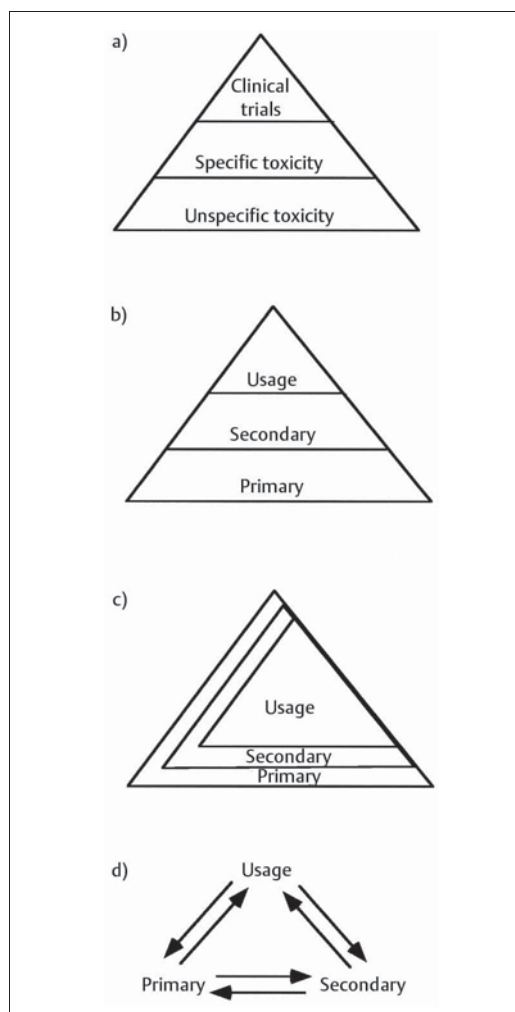


Fig. 14.3 Schemes for testing biocompatibility. (a) The oldest scheme used “unspecific” toxicity tests first, followed by “specific” toxicity tests, and then by clinical trials. Only materials that passed one level were tested further. Unspecific tests were those that were not directly relevant to the use of the material. (b) This scheme employs primary, secondary, and usage tests, and it is still commonly employed today. The scheme differs from (a), because it emphasizes many cellular reactions in addition to toxicity. As in (a), each level of the test screens for the tests above it. Primary tests measure basic biological properties such as toxicity or mutagenicity of the material. Secondary tests assess more advanced properties such as allergenicity. Usage tests are equivalent to clinical trials. (c and d) Newer schemes for biocompatibility testing recognize the need to use several types of tests together and that the evaluation of biocompatibility of a material is an ongoing process

into “primary, secondary, and usage tests,” illustrated in Figure 14.3b. This newer scheme expanded the scope of the tests beyond toxicity. Primary tests consisted of general cell toxicity, systemic toxicity in animals, bacterial mutagenic tests, and other types of *in vitro* tests. Secondary tests consisted of tests to measure allergy, mucosal irritation, and inflammation. Usage tests were equivalent to clinical trials. Both schemes used the pyramid approach as a screening procedure. Only materials whose tests passed the lowest level of the pyramid were considered for further testing. Likewise, only materials whose tests passed the second tier were considered for clinical trials. Although efficient in time and costs, these schemes ignored the reality that the initial tests frequently resulted in false positive and false negative responses of the materials.

Newer schemes have been developed that reflect the complexity of biocompatibility testing of materials, as displayed in Figures 14.3c and d. Both of these schemes recognize several key points. First, all three types of biocompatibility tests continue to be useful throughout the evaluation of a material and during its clinical service. An *in vitro* test may be useful in the initial stages of material development to “screen in” promising materials, but it may also be useful to investigate a specific biological response observed during clinical trials or after introduction into the market. Second, both schemes recognize the danger in “screening out” a material with a single type of test. Finally, both schemes recognize that the evaluation of the biocompatibility of a material is an ongoing process that evolves during clinical experience with the material. In particular, the practitioner must keep this last point in mind.

Relevance to the Dental and Orthodontic Practitioner

How are these rather theoretical and technical aspects of biocompatibility useful to the orthodontic practitioner? Several points are appropriate. First, the practitioner must be careful when evaluating sales literature claiming biocompatibility for a material. Marketing claims must be scrutinized carefully. What tests were used to evaluate the material? Is the company assuming that the new material will

behave like a previous material? Second, new materials may be marketed with little clinical experience, and companies may rely heavily on *in vitro* and animal tests. In these cases, the practitioner must try to understand what tests have been performed and their relevance to the clinical use of the material, keeping in mind the limitations and pitfalls outlined above. Even if clinical trials have been done, the practitioner must remember that clinical trials may be only one to two years in duration. The service life of many biomaterials is longer than this, and the long-term effects cannot be

assessed in short-term trials. Third, the practitioner must remember that the biological evaluation of materials is an ongoing process. As more knowledge is gained, opinions about safety and risk may also change, and it is dangerous legally and ethically to ignore new developments. Finally, the decision of a practitioner to use a new material is ultimately a risk-benefit decision that each practitioner must make for himself or herself, hopefully based on published evidence by unbiased researchers that considered the needs and risk tolerance of their patients.

Standards and Biocompatibility Testing

Why have standards?

The need for standards in biocompatibility testing stems from the extreme complexity of these types of tests. Because of this complexity, the outcome of any test for biocompatibility depends heavily on the design of the test. Biological tests, in particular *in vitro*, animal, and usage tests, have a myriad of variables to be manipulated and controlled. For example, one study has shown that the choice of cell lines is of tremendous importance in measuring the simple toxicity of metal ions that might be released from metallic orthodontic materials. Depending on the choice of cell line, the apparent toxicity of the metals may vary by 10 times or more. Similar problems can be shown for animal or usage tests. Since the conclusion about the safety of a material relies upon the results of these tests, standardization is the only way currently known to help reduce the confusion and compare materials fairly.

Standardization of tests is also important to allow comparison of different materials. For example, the outcome of a simple toxicity test for a biomaterial may be manipulated by changing the ratio of the number of cells to the amount of material. A toxic result may be obtained if the number of cells is low relative to the amount of material, or the opposite result may occur if the number of cells is high relative to the amount of material. For this reason, standards stipulate an accepted range for this ratio. This practice allows fair comparison of different materials. The ability to compare

materials is a powerful tool, because a new material may be compared with a material with known clinical success. However, one is still plagued with the problem of the relevance of the test. For example, an animal test may show that a new ceramic material for orthodontic brackets is as good as or better than a traditional stainless steel material in a subcutaneous implantation test. However, since the implantation test has little relevance for the type of service of the bracket, one must question whether this comparison is useful.

A host of standards exist for biocompatibility testing, administered by different governmental agencies worldwide. Standards for biological testing have been published by the American Dental Association (ADA specification no. 41), the International Organization for Standardization (ISO standard no. 10993), the European Union (EN standards), the American Society for Testing and Materials (ASTM standards), the British Standards Institution (BS standards), and many others. There is significant overlap among the standards of these various organizations. Each of the standards contains details about the philosophy of the standard, the biological aspects it considers, and the types of tests it requires. Knowledge about the specifics of the standards is well beyond the need of orthodontic practitioners. However, to use the results of standards testing in his or her decision-making about the safety of materials, the practitioner needs to understand several concepts about and weaknesses of biological standards.

Concepts and Weaknesses

The orthodontic practitioner must be aware of the difference between a device and a drug, because these two types of agents are treated entirely differently in standards documents. The definition of a medical device is itself quite complex, but a medical device can be roughly defined as an instrument or material used in medical practice that does not achieve its purpose in the body by a chemical action. Drugs, on the other hand, achieve their purpose through chemical or biochemical action on the body tissues. The scope of medical devices is extremely diverse and may include everything from an orthodontic bracket to a heart valve to the software controlling a computer to measure blood pressure. The important point is that orthodontic materials (and almost all dental materials) are considered devices and therefore do not need to fulfill the additional requirements imposed on drugs. The biological standards mentioned in the previous paragraphs all apply to devices but not to drugs.

The biological requirements for a material will depend on how it is exposed to the body. ISO standard no. 10993 divides (Table 14.2)

exposure conditions into noncontact devices (not relevant to orthodontic materials), surface-contacting devices (orthodontic brackets and wires), externally communicating devices that penetrate the mucosa or hard tissues (dental restorative materials), and implanted devices that are completely embedded in tissue (not relevant to orthodontic materials directly). Testing requirements will also depend on the duration of the contact with the body. ISO standard no. 10993 categorizes contact as limited (< 24 hours, *e.g.*, impression materials), prolonged (24 hours to 30 days), and permanent (> 30 days). Thus, many orthodontic materials are classified as permanent devices, despite the practitioner's view that they are really temporary in terms of the patient's lifetime. For example, an orthodontic retainer is a permanent device according to the ISO. Finally, testing requirements will depend upon which tissues in the body the material will contact.

Most biological standards do not rely on a single test for the assessment of biocompatibility. Rather, a series of *in vitro*, animal, and usage tests are likely to be stipulated. Furthermore, most standards documents do not list specific tests that must be used to gain ap-

Table 14.2 Exposure factors that are important for the selection of biocompatibility tests (according to the International Organization for Standardization)

Factor	Possible Choices	Orthodontic Examples ^a
Duration of exposure	Limited (< 24 hr) Prolonged (24 hr–30 days) Permanent (> 30 days)	Alginate Impression NA (not applicable) Orthodontic brackets Acrylic retainers Orthodontic wires
Surface device	Skin Mucosal membrane Breached or compromised surface	Headgear supports Acrylic retainer NA (normally)
Externally communicating device	Blood path – indirect Tissue-bone-dentin communicating Circulating blood	Orthodontic brackets and wires NA (normally) NA (normally)
Implanted device	Tissue-bone Blood	NA (except orthognathic surgery devices) NA (except orthognathic surgery devices)

proval. The standard will give guidelines based on the type of contact, duration of contact, and tissues contacted (Table 14.2). For example, an orthodontic wire would be classified as a permanent (> 30 days contact), surface-contacting (does not penetrate the oral mucosa or hard tissues) device that contacts the oral mucosa and hard tissues. For these conditions, the ISO would require *in vitro* toxicity tests, animal tests for systemic toxicity, animal tests for mucosal irritation, allergic sensitivity tests, and tests for genotoxicity. If the wire were likely to penetrate the oral mucosa (which might occur on some occasions), then the device would be considered an externally communicating device, and would require animal implantation tests and perhaps usage tests. The exact selection of tests is often left to the company, but the company must successfully defend its choices to the experts on the evaluating board. In this way, the standards are flexible enough to encompass the diverse nature of dental devices. However, it leaves the practitioner with the responsibility of understanding exactly how the orthodontic material gained approval and whether this strategy was relevant to him or her.

Another concept that is crucial to standards and dental devices is that of the “grandfather clause”. A material can be approved for use if the manufacturer can show that the material’s composition and use are “substantially equivalent” to an existing material’s use and composition. For example, a new orthodontic bracket that has the same composition and general use as existing brackets, but a different shape, could be approved for use without additional biological testing, as long as the shape did not influence the biological performance. Companies are eager to use the grandfather clause for dental materials, since it avoids expensive and time-consuming biological tests. However, the practitioner should always keep in mind that the judgment of “substantial equivalence” is ultimately a subjective one, and the practitioner must decide whether he or she agrees with this decision.

For all their usefulness, biological standards have several weaknesses that limit them. First, there is not agreement among the various standards about procedures and requirements. In a sense, standardization of the standards is badly needed! There have been attempts to provide uniformity among the standards, but significant differences still exist. Second, the large bureaucracy involved in formulating and publishing a standard often results in the tests in the standard lagging behind current philosophies or technical abilities. Thus, standards may contain tests that have been shown not to be useful or that have been replaced in the literature by more expedient tests. Third, the practitioner must remember that standards are the result of a compromise among academic, industrial, other technical, and lay people. A requirement for a minimum percentage of nickel in an orthodontic alloy was arrived at through complex and prolonged negotiations among these groups. The percentage may or may not have any real biological relevance.

Relevance to the Dental and Orthodontic Practitioner

Biological standards are relevant to the orthodontic practitioner because they can have great influence upon which materials will be available for orthodontic practice and how the materials are marketed. The practitioner must try to be aware of which standards were required to bring the material to the market, and must keep in mind the practical weaknesses and limitations of any standard. The practitioner should also be aware that nonstandard tests may be used (appropriately or inappropriately) to market a material. Most importantly, the practitioner must decide on the safety and use of a material, based upon his or her own philosophy of practice. Ultimately, the responsibility for using a material rests with the practitioner, and the selection of a material must reflect that fact.

Key Factors in Assessing Biocompatibility

The remainder of this chapter will use the issue of the potential estrogenicity of dental resins to demonstrate many of the principles of biocompatibility discussed in previous sections. The practitioner should remember that two key factors will always be relevant when discussing the biological effects of a material: (1) whether the material releases any of its components, and (2) whether the released components have any relevant biological effects. The issue of estrogenicity of dental resins is especially relevant to orthodontics because orthodontists use resin-containing materials as cements or sealants in young patients who would be especially susceptible to any estrogenic effect. This is therefore an emotionally charged issue that demonstrates well the principles of biocompatibility.

What is Released from the Resin-Based Material?

Dental resins are initially mixtures of low-molecular-weight organic molecules that polymerize into a solid mass when cured by light or chemical means (Chapter 9). In an idealized viewpoint, if the polymerization were complete, the set resin would be one continuous macromolecule that could not release anything into the body, unless some of the covalent bonds of the polymer were broken. In practice, however, the polymerization is not complete, and small amounts of the starting products are at least theoretically available to be released into the body.

There is little doubt that cured dental resins release components into the body. Reports of early tests that used mass loss to measure component release estimated that the release was short-lived (48 hours). However, studies using HPLC (high-pressure liquid chromatography) have demonstrated that components are released from resins for several weeks to months. Furthermore, studies that measure cytotoxicity of cured resin materials have shown that cytotoxicity continues for weeks to months, implying that substances continue to be released from the resins. Other studies indicate that within the bulk of a set dental resin there is a

large reservoir of uncured material that at least has the potential eventually to be released into the body.

Determining the identity of the substances released from resin composites is a complex issue, because the HPLC methods used to detect release are difficult to use for positive identification. HPLC will indicate the release of chemicals, but determining the identity of these chemicals is not straightforward. This problem worsens as the amount of release becomes smaller. Nevertheless, several studies indicate that dental resins release Bis-GMA (an oligomer of the resin), TEGDMA (a diluent), and several other major components. The release of low levels of other components or impurities in the starting products is not clear. High-resolution HPLC techniques may improve our knowledge in this area.

Thus, dental resins at least have the potential to cause adverse biological reactions because they are known to release low levels of their components, and at least some of these components are cytotoxic. The controversy surrounding the estrogenicity of dental resins has resulted from a single article published by Olea *et al* in 1996 that stated that some dental sealants released bisphenol A into the saliva at significant concentrations. This article further hypothesized that bisphenol A had estrogenic properties at the released concentrations and was a plausible xenoestrogen in the body. Bisphenol A (Fig. 14.4) is a small organic molecule that is used with glycidyl dimethacrylate to synthesize Bis-GMA. It is not added directly to most dental resin materials, but is an impurity in the Bis-GMA that is incorporated in the resin formulation. Bisphenol A is also used in the manufacture of other types of resins not used in dentistry. Fears about the

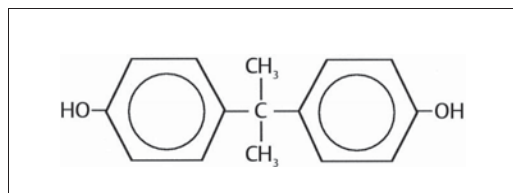


Fig. 14.4 Bisphenol A (BPA), an organic molecule with known estrogenic properties

safety of dental resins, especially in children, have prompted regulatory agencies to begin to investigate this issue. No standard currently applies to estrogenic effects of dental resins.

So the questions of interest in this debate became: (1) whether dental resins release bisphenol A and (2) whether bisphenol A is truly estrogenic. Additional investigations after the Olea *et al* study failed to detect bisphenol A release from dental sealants or other dental resin materials. A recent study has reported the presence of extremely small amounts of bisphenol A in some dental resins, which are probably trace contaminants of chemicals used to manufacture the resins.

What are the Effects of the Released Components of Resins?

If bisphenol A is released from dental resin materials, then one must ask whether it has any adverse biological effects under the conditions of its release. Although most studies indicate that the release of bisphenol A is minimal at most, a close look at this issue is instructive.

There is little doubt about the estrogenicity of Bis-GMA. Some of the original work reported by Olea *et al* in 1996 has been supported by other research and has shown that bisphenol A can act as a weak estrogen in cell culture. However, the potency of the estrogenic effect is probably 1000 times less than that of naturally occurring estrogen (Fig. 14.5). The *in vivo* effects of bisphenol A are less evident and are under study. Thus, the question becomes whether the minuscule amounts of bisphenol A that *might* be released from dental resins have any biological relevance. Although the answer is unknown at present, there is no reason to believe that the levels of bisphenol A that are present in resins pose any biological threat to patients or dental staff.

Relevance to the Dental and Orthodontic Practitioner

The issues concerning the estrogenicity of dental resin materials illustrate several important points about the principles of biocompatibility. First, the release of components from

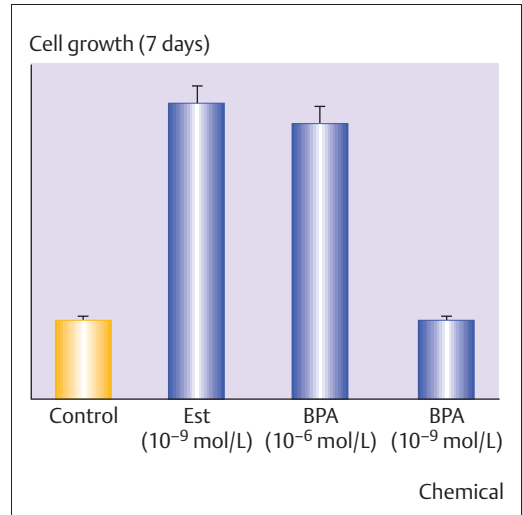


Fig. 14.5 Graph illustrating the estrogenic potential of bisphenol A (BPA) versus endogenous estrogen (Est). Estrogenic materials cause increased cell growth in cells that are responsive (breast cancer cells in this experiment). Control conditions caused normal cell growth. Both estrogen and bisphenol A increased cell growth over controls and have therefore been called estrogenic. However, estrogen acted at 10^{-9} mol/L while the BPA was 1000 times less potent, causing growth at 10^{-6} mol/L. BPA caused no cell growth in the estrogen-sensitive cells at 10^{-9} mol/L.

materials is generally a necessary, but not a sufficient event to cause adverse biological effects. Bisphenol A cannot be estrogenic if it is not released, but even if it is released, an estrogenic effect is not assured. Second, biological effects of released components are dependent on their form, concentration, and location. Bisphenol A is weakly estrogenic in a culture of specialized cells, but its *in vivo* effects are far less clear. Even if small amounts of bisphenol A are released from dental resins and cements, it seems unlikely that these concentrations are high enough to have the estrogenic effects that have been purported.

Third, the regulatory mechanisms are always lagging behind current issues. The fear about the estrogenicity of resins has prompted regulatory agencies to investigate these questions, but the research to answer these questions will be years behind the fears of the patients. The problem is exacerbated by a lack of standardized tests for the estrogenic effects of materi-

als. Thus, the practitioner must answer questions from patients without the guidance of regulations or in-depth research. The practitioner must evaluate existing research himself or herself, understanding as much as possible about what tests were performed, what limitations these tests have, and what tests need to be conducted in the future. This quandary is common with biocompatibility issues, and is the reason the technical aspects of biocompatibility evaluation have been presented in this chapter.

Finally, the estrogenicity issue illustrates the principle that decisions about the safety of materials are as much philosophical as scientific.

Because no material can be proved 100% safe, the decision to use materials in the mouth is one based on a balance between risks and benefits. Ultimately, the practitioner must determine whether the benefits to the patient outweigh the risks in his or her own mind. To avoid all risk is to deny the patient the tremendous benefits that orthodontic biomaterials have to offer. To assume too much risk may harm the patient and put the practitioner at legal risk. The technical tests and data can aid the practitioner in this decision, but the decision is ultimately a philosophical one about how much risk is to be assumed.

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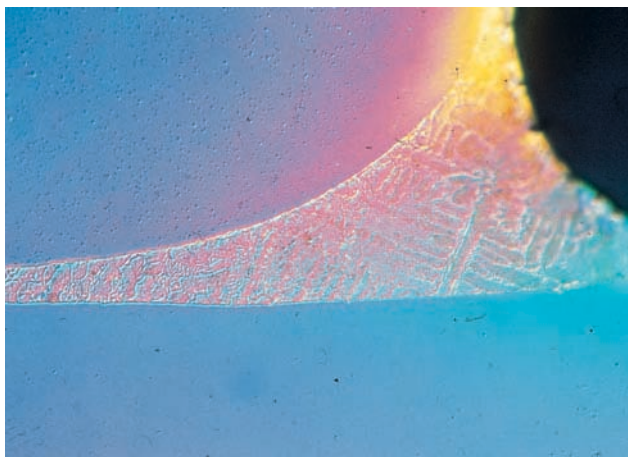
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15 Allergic Reactions and Safety Concerns

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Transverse section of a bracket, with the base down. Solder is visible in the triangular space. (Original magnification $\times 40$)

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Introduction

During orthodontic treatment the oral tissues may be exposed to fixed metal appliances such as molar bands, brackets, transpalatal bars, facebows, archwires, and retainers with auxiliary devices such as springs and hooks. Resin-based materials in bonding systems and removable appliances, along with ceramic brackets, add to the range of orthodontic biomaterials. In addition, polyurethane elastomers and headgears of different composition belong to the orthodontic armamentarium. Altogether, orthodontic appliances can comprise a considerable surface of biomaterials in contact with the oral mucosa for a prolonged period of time, and portions may also extend to the skin of the chin, cheeks, and neck. Fixed

orthodontic devices manufactured from base metal alloys are more prone to corrosion than those of noble metal alloys, and removable devices are often produced by chemical polymerization ("cold-curing technique"), facilitating dissolution phenomena and leaching of unreacted components, as compared with heat-cured products. The present chapter will discuss adverse reactions following the uptake of components derived from orthodontic appliances. Consideration of the adverse potential associated with orthodontic biomaterials will include a discussion of occupational hazards. The allergenic role of nickel will be emphasized.

Decomposition and Absorption Mechanisms

The Oral Environment

The principal factor in the oral environment is the saliva, containing both organic species and inorganic components such as chloride and phosphate ions. Although saliva is a well-buffered secretion, pH variations occur as a result of food and drink intake and microbial activity. Intraoral devices will therefore be subjected to chemical and physical environmental factors such as pH fluctuations, electrochemical activity, temperature differences, and abrasive and mechanical forces, all contributing to material deterioration. Depending upon the nature of the material (metallic or nonmetallic), these processes are called corrosion or degradation.

Corrosion and Degradation

As previously discussed in Chapter 1, *corrosion* is the term for an electrochemical reaction between a metallic material and its surrounding environment. In the oral cavity, corrosion takes place by release of positive metal ions from orthodontic alloys to form more stable compounds such as chlorides, sulfides, and

oxides. Such thermodynamically unstable metals as iron, nickel, chromium, molybdenum and titanium are important component elements of archwire alloys (Chapter 4) and metallic brackets (Chapter 7). In addition, orthodontic solders are often alloys of silver, copper, and zinc, sometimes with traces of nickel, chromium, and iron. There are also solders based upon nickel or gold as the main component element.

The release of metal ions is not directly proportional to the amount of each metal in the alloy. For example, NiTi archwire alloys containing 54 wt% nickel have been found to release negligible amounts of this element because these alloys are highly corrosion resistant. Corrosion phenomena are increased by internal stresses in the metal appliances, by the inhomogeneous structure of the alloy, and by different metals coming into contact. A smooth, homogeneous surface makes an orthodontic appliance less prone to corrosion, whereas inhomogeneous soldered connecting points between different parts of an appliance are highly susceptible to corrosion. Figures 15.1 and 15.2 illustrate the type of contact that can arise between different alloys in a facebow and a bracket, and their corresponding solders.

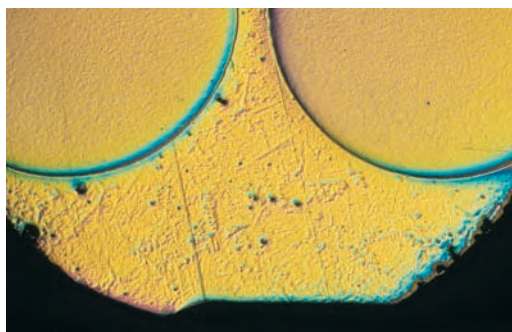


Fig. 15.1 Transverse section of an inner and outer facebow connected with solder. Elemental analysis (EDS) showed compositions of 71 % Fe, 19 % Cr, 8 % Ni, and 1 % Mn for the facebow, and 60 % Ag, 23 % Cu, and 17 % Zn for the solder. (The principles of EDS analysis are discussed in Chapter 3.) Original magnification $\times 5$

Recycling of stainless steel brackets after high-temperature heating may make the steel less corrosion resistant. Corrosion phenomena apparently do not diminish the mechanical properties of the brackets to any significant extent, but they contribute to the release of foreign substances that may have biological implications. The presence of passivating surface oxide films such as chromium oxide on stainless steel (Chapter 4) slows the corrosion, whereas abrasion, polishing, high acidity, or high chloride concentration contributes to the loss of these passivating films.

Polymeric materials are subject to *degradation* as a result of the combined chemical,

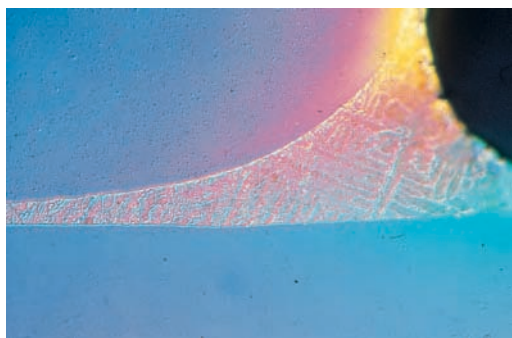


Fig. 15.2 Transverse section of a bracket, with the base down. Solder is visible in the triangular space. Original magnification $\times 40$

microbiological and wear processes that occur in the aggressive environment of the oral cavity. Residual double bonds in the backbone of pendant side chains of the macromolecule are attacked by thermal, mechanical, chemical, or photochemical mechanisms. Release of oxidation or hydrolysis products occurs, along with residual monomers and components belonging to the polymerization process (Chapters 9 and 10). These components may include chemical initiators, activators, and inhibitors, or their degradation products. In addition, resin-based removable appliances may contain leachable plasticizers originally incorporated to improve physical properties. Orthodontic adhesives add to the repertoire of leachable organic substances, together with remnants of coupling agents from inorganic fillers of orthodontic composites that have been subject to hydrolytic degradation. The use of alginate or other impression materials represents additional possibilities of contact with other polymerizing materials and chemical additives connected with polymerization processes. In addition, the use of orthodontic latex elastics and latex gloves results in exposure to components related to latex. Components leached from latex are chemically active substances with potentially haptenic properties (see later).

It follows that the pool of xenobiotic substances derived from orthodontic treatment in the oral cavity is a mixture of inorganic ions and compounds, together with organic components.

Some products are surface layers in the form of tarnish and passivating films, and other products are more soluble compounds released into the neighboring mucous or salivary flow. Most species are of low molecular weight, and their concentrations in the oral environment are difficult to assess. In addition, the origin of certain products may be difficult to distinguish from that of similar species derived from food, cooking utensils, or the respiratory environment.

Routes of Entrance

Volatile substances from resin-based bonding materials or removable devices may represent an occupational hazard for orthodontic personnel by respiratory tract and conjunctival ab-

sorption. Otherwise, the clinically relevant route of entrance for chemical species associated with orthodontic treatment is through the oral *mucosa* or the *skin* of patients. Orthodontic devices are placed in intimate contact with the surface of the oral mucosa and, for some devices, the skin and the mucocutaneous transitional zone of the lips. Since the appliances cannot always be anatomically shaped to perfection, the probability of (perhaps sub-clinical) frictional injuries of the movable parts of the soft tissues always exists. Despite these circumstances, the soft-tissue contact is generally uneventful. The exceptions are adverse effects following the uptake of released foreign substances.

Mucosal and Skin Uptake – Differences and Similarities

In principle, all foreign substances have to pass the membranous barriers of epidermal or epimucosal cells to reach the blood and lymph capillaries. The passage takes place by passive diffusion, depending upon the chemical nature of the foreign molecule, the concentration gradient, and the thickness and surface area of the membranes. Lipophilic, nonpolar xenobiotics diffuse by dissolving in the phospholipid membranes, whereas small, hydrophilic, or polar molecules are transported by diffusion through the aqueous membrane pores. For anatomical reasons, diffusion through the lipid phase of membranes is the most important transport mechanism.

In *skin* the xenobiotic molecules must pass through multiple layers of epidermal cells. Not counting the small portion of nonkeratinized epithelial tissue located adjacent to sweat glands and hair follicles, the outer layers of the epidermis are composed of denucleated, biologically inactive, keratin-filled and dehydrated cells with thickened cell membranes. The physical state of this tissue results in a slower diffusion rate for a chemical species than does nonkeratinized epithelium. The inner layers of the epidermis do not provide a similar diffusion barrier. Despite these factors, foreign substances are transported across skin, and increasingly so if the keratinized outer layers are removed or injured after contact with soaps and detergents. Occlusion of skin with ban-

dages, tapes, or gloves has similar effects, all explained by increased hydration and by disintegration of the keratin molecules.

The permeability of the nonkeratinized parts of oral mucosa is comparable to that of hydrated skin. The absence of the physical barrier of the keratinization is partly compensated by a layer of mucus, consisting of acid, phosphated or sulfated glycoproteins, and lipid produced by the small salivary glands. The mucus adheres well to soft and hard tissues, and helps retain fluid, inorganic ions, and salivary proteins in place. It is conceivable that the mucinous glycoproteins also bind trace substances leaching from orthodontic biomaterials, but definitive experimental data in this area are not available. Although the mucous flow diminishes the contact time between the oral mucosa and the absorbants, the constant moisturizing of the oral mucosa facilitates absorption. The connective tissue is not considered a diffusion-limiting factor in either tissue. The antigen-presenting Langerhans cells are present at a higher concentration in the suprabasal *epidermal* layers as compared to the corresponding *mucosal* layers.

Toxicodynamic Considerations

Most components leaching out from orthodontic devices would be toxic if present at concentrations exceeding a threshold limit dose. *Nickel* imparts useful properties to many orthodontic alloys (Chapters 4 and 7), although it is a powerful toxicant and a carcinogen. Nickel is present in small amounts in animal, fish, and vegetable foods, and in the air, depending upon the degree of urbanization. The daily human absorption of nickel from food is approximately 300–500 µg. In comparison, the *in vitro* release of soluble forms of nickel from a simulated full-mouth orthodontic appliance into 0.05% saline solution is about 40 µg. The corresponding data for chromium are 5–100 µg taken up from food and 36 µg released from the orthodontic appliance in the form of nonsoluble passivating surface precipitates. Other *in vitro* studies have indicated similar concentrations. Attempts to determine the actual concentration of nickel in the saliva of orthodontic patients have been inconclusive, apart from the finding of extremely low concentrations. The blood level

of nickel is not affected following the insertion of orthodontic appliances. Other components from dental materials in the oral cavity are also present in trace amounts, if measurable. Based upon these considerations, a systemic toxic effect of nickel – or from other components derived from metallic orthodontic appliances – is highly unlikely. The potential for side effects due to components derived from metallic orthodontic materials is limited to dose-independent *allergic reactions*, although it has

been suggested by Swedish dermatologists that *nickel* derived from dental biomaterials or other sources may play a part in the development of the chronic fatigue syndrome (CFS). CFS patients have been shown to have a high frequency of immunological abnormalities, such as nickel allergy. A possible psychoneuroimmunological mechanism would include lymphocyte activation by the nickel, with the release of various cytokines able to cause generalized symptoms.

Allergic Reactions

General Characteristics

An adverse reaction following contact with subtoxic doses of foreign substances is referred to as *hypersensitivity*. Hypersensitivity reactions comprise three different mechanisms: allergy, intolerance, and hyperreactivity. Intolerance reactions are mostly related to foodstuffs and inborn errors of metabolism. Hyperreactivity responses are often related to volatile irritants. *Allergy* is an acquired condition resulting in an overreaction upon contact with a foreign substance, and arises from a genetic predisposition and previous sensitization from exposure to the substance. Allergic reactions may include asthma, rhinitis, conjunctivitis, urticaria, intraoral and systemic symptoms, and eczema brought about by several immunopathological mechanisms. These mechanisms are most often categorized into four groups, types I to IV, of which the *immediate reaction* (type I) and the *delayed reaction* (type IV) have relevance to orthodontic biomaterials.

The Type I “Immediate” Reaction

The type I reaction often occurs a few minutes after contact with the antigen in a sensitized individual. The antigen combines with IgE antibodies located on mast cells or basophilic leukocytes, and releases mediators such as histamine and prostaglandins, leading to increased capillary permeability, contraction of smooth muscle, or disturbances of endocrine function. Depending upon the sensitized organ, the re-

sulting symptoms may be asthmatic seizures, swelling of the mucosa of the throat and eyes, urticaria, contact urticaria or worse decreased blood pressure and anaphylactic shock. The type I reaction depends on sensitization with full antigens. Potential allergenic substances derived from orthodontic biomaterials are small molecular *haptens* that are unable to induce immune reactions without combining with tissue proteins. This fact limits the type I allergens in orthodontics to residual proteins from latex products (gloves) that are able to act as full allergens. The type I hypersensitivity may be tested by allergists using a skin prick test that includes intradermal injections of different concentrations of the suspected allergen. The resulting wheal and flare are compared with the responses after injection of negative and positive control substances, such as saline and histamine.

The Type IV “Delayed” Reaction

The most common reaction associated with dental materials is the type IV reaction, referred to as “delayed hypersensitivity”, because it is observed 24–48 hours after the exposure. With the delayed reaction the hapten is absorbed by the skin or mucosa and binds to certain proteins associated with the Langerhans cells to form a complete antigen. By means of the Langerhans cells the antigen is brought in contact with the T lymphocytes of the regional lymph nodes, resulting in the formation of activated, “custom-made” T cells. These cells are brought into the blood circulation by lymph

vessels and may therefore be present in peripheral areas. This is the sensitization phase.

Upon new exposure, the allergen may again be transported from the site of entrance by the Langerhans cells as before. The new contact between the allergen and the activated, specialized T cells releases inflammatory mediators, resulting in further attraction of T cells and causing tissue damage. The tissue reactions may comprise intraoral diffuse red zones, blisters, and ulcerations extending to the perioral area, and are referred to as *allergic contact mucositis* or *dermatitis*. For the reasons indicated, the reactions are not necessarily limited to the exposure site, although most reactions are. Eczematic and urticarial reactions of the face or more distant skin areas occur. This pattern is different from the clinical expression of *irritant contact dermatitis* occurring at the site of exposure. *Irritant* and *allergic* contact dermatitis may be difficult to distinguish, particularly when occupation-related disorders are encountered.

The sensitization process may have taken place a short time (weeks) or a long time (years) prior to the hypersensitive reaction. It should be remembered that the sensitization may be the result of exposure to haptens derived from other sources than orthodontic materials. An example is nickel sensitization by custom jewelry or piercing devices, representing an increased hazard for allergic reactions when using nickel-containing alloys in orthodontic treatment.

The assumed causes of delayed allergic reactions may be verified or disproved by epicutaneous tests. The epicutaneous tests ("patch tests") are performed by taping to skin the suspected substances dissolved in an adequate medium, such as petrolatum, alcohol, or water. After a predetermined period of time, e.g., 48 hours, erythematous reactions are evaluated according to a scale ranking from negative to extremely strong or irritative. The concentration of the test substance that enables the detection of an allergic reaction without provoking a local chemical irritation is a critical matter. Commercial test kits have been developed for testing of dental materials-related reactions.

It is accepted that a positive patch test indicates the presence of an allergic reaction to the tested substance, but the patch test is not

conclusive regarding a causal relationship between the suspected allergen and the reaction. It is possible to have a positive patch test to a certain dental material and still have no adverse reaction to dental restorations containing the material. The inverse situation is also possible.

It has been shown that sensitization by way of the oral mucosa is more difficult to accomplish than by way of the skin, presumably because of the difference in the concentration of Langerhans cells. In addition, the delayed allergic reactions are not as easily provoked on the surface of the mucosa as on the surface of the skin. This is why epidermal and not epimucosal patch tests are used also in cases of intraoral reactions. It is not clear whether possible hapten-protein complexes specific to the oral mucosa are "lost" by skin testing.

Atopy

Atopy is defined by allergists as a constitutional predisposition for IgE-based hypersensitivity reactions, often induced by contact with widely distributed allergens such as pollens, animal proteins, dusts, fumes, and food ingredients. However, there is no general agreement on the criteria for determining atopy. The reactions include histamine-mediated hay fever, asthma, gastrointestinal symptoms, or skin rashes (atopic dermatitis), reflecting antigens that have been inhaled or ingested. Atopy is of specific importance in childhood, affecting as much as 10% of the population. Many studies have shown an increased risk for atopic individuals to acquire irritant contact dermatitis. Experimental studies indicate that the risk may be limited to cases of active atopic dermatitis. The relation between allergic contact dermatitis and dermal atopy is unclear, with the exception that all factors affecting the integrity of epidermal tissue are of importance in the sensitization process.

Potential Allergens

Potential allergens in orthodontic practice can be divided into metal salts derived from the fixed devices, monomers, cross-linking agents, and polymerization chemicals associated with

Table 15.1 Sources and nature of allergens associated with orthodontics

Fixed Devices	Removable Devices and Bonding Systems
Metals, such as: Chromium, Cobalt, Nickel, Copper, Titanium, Silver	Monomers, cross-linking agents and polymerization chemicals, such as: Methyl methacrylate (MMA), Triethylene glycol dimethacrylate (TEGDMA), Ethylene glycol dimethacrylate (EGDMA), 1,4 -Butanediol dimethacrylate, 2-Hydroxyethyl methacrylate (HEMA), Epoxy resin, Activators, Inhibitors, Softeners
Fabrics in Extraoral Equipment	Latex-Associated Products
Coloring or preparatory chemicals	Vulcanization chemicals
Formaldehyde	Residual proteins
Colophony	“Powdering” components

bonding systems and removable appliances; latex-related components from gloves; and miscellaneous factors. Table 15.1 lists some examples of allergens in each category. Most of the examples of allergens are extracted from a commercial epidermal test kit relevant to dental materials. Apart from the residual proteins of latex, all listed ingredients are haptenic and cause delayed hypersensitivity. Metal allergy is relevant to patients and dental personnel. The most frequent sensitizers are nickel, chromium, and cobalt, in that order. The resin-based ingredients comprise a series of chemically active organic components. Allergic reactions are possible for both patients and operators. A ranking of the sensitizing capacity or of the incidence of reactions in orthodontics

caused by substances in this group is not possible. Reports from occupational medicine indicate that the MMA (methyl methacrylate) monomer (Chapter 9) is of the most concern.

The allergenic components of natural latex comprise chemicals related to the vulcanization process, residual proteins from the rubber tree, and chemicals associated with the powdering of gloves. Latex allergy in orthodontic patients is associated with exposure to the latex gloves worn by the orthodontist. Type I immediate reactions have already been described.

Extraoral orthodontic equipment may include fabrics containing coloring or other preparatory chemicals that may also produce delayed allergic reactions by contact with the skin of the chin and neck.

Adverse Patient Reactions

Observed Reactions

Of 10 cases of adverse reaction reported from a Norwegian orthodontic clinic in 1984, nine were skin reactions located at the corner of the mouth or other skin areas with appliance contact. In one case, eczema was present at distant locations as well. Only one patient showed intraoral lesions. As judged by epicutaneous tests, *nickel* was the most frequent causative factor. However, reactions to cobalt and

ethylene glycol dimethacrylate (Chapter 9) were also found. Figures 15.3 and 15.4 illustrate reactions of this kind encountered in orthodontic practice.

A questionnaire study among Norwegian orthodontists in 1989 confirmed that extraoral reactions such as redness, itching eczema, soreness, fissuring, and desquamation were by far the most frequent responses, and were often attributed to metal parts of the orthodontic appliances. Some reactions were attributed to non-



Fig. 15.3 Red dermal lesions at the corner of the mouth and cheeks of a 12-year-old nickel-sensitized girl with intraoral and extraoral orthodontic appliances. The dermal reactions cleared up after coating of the metal parts with sheet thermoplastics

metallic items such as head caps, neck pillows, and extraoral elastics. Oral reactions were described as redness, swelling, itching, and soreness of the lips and oral mucosa; or redness, swelling, or inflammation of the gingiva and palate. The reactions were assumed to arise from the resin and metal parts of fixed and removable appliances and from rubber elastics: A tentative prevalence of reactions was estimated at that time to be about one out of 100 orthodontic patients. The reactions experienced by the patients probably comprised both irritant and hypersensitive responses. In this type of study the proportion of true allergies could not be determined.

Nickel has attracted the most attention as a potential sensitizer in the odontological setting. The extensive use of nickel-containing base

metal alloys has necessitated a thorough scrutiny of the allergenic role of nickel in orthodontics.

Nickel Sensitization

Nickel is the principal sensitizer in the Scandinavian population, as recorded by dermatological units. Nickel allergy is especially frequent in the female population, approaching 20% among young Scandinavian girls. The incidence of nickel allergy is significantly lower, about 2–3% but increasing, in the young male population. The large-scale sensitization process is brought about by the ubiquitous presence of nickel in metal articles for everyday use, most importantly by the presence of nickel in various appliances or items that are in contact with the skin. Over the years, the sensitization process has been changing with changing fashions. Nickel-containing metal suspenders and clothing buckles, wristwatch-fastening appliances, nickel-containing eyeglass frames (obscured by gold and silver plating), and costume jewelry have taken part in the development of nickel allergy, facilitated by sweat and other skin moisture. Ear piercing has brought an extra dimension to nickel sensitization because plasma and inflammatory exudates increase the tendency for metal corrosion, and because the metal contact takes place in an unepithelialized tissue channel. In addition, the piercing fad has spread to many other locations of the body and to males, further increasing the sensitizing potential. The sensitization often takes place at an early age. Investigations of

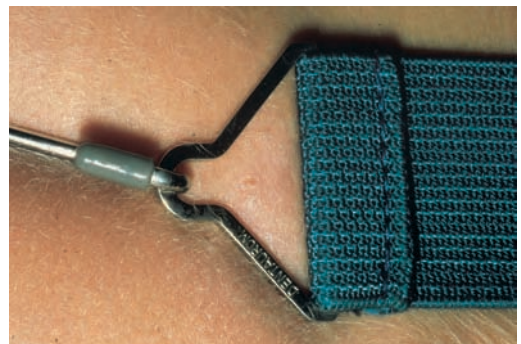


Fig. 15.4 (a) Eczema of the cheek in a 12-year-old nickel-sensitive girl, corresponding to the buckle for headgear. (b) Elemental analysis showed that the buckles contained nickel-plated brass

an unselected Danish population of both sexes and all ages indicate that the sensitizing effect of piercing is not sex-specific or age-dependent.

Fundamental questions exist about the role of nickel from orthodontic appliances in the nickel hypersensitivity pattern. Is the nickel released into the oral cavity able to sensitize an individual, or are nickel reactions associated with orthodontic treatment limited to previously sensitized patients? Might oral nickel exposure such as that from orthodontic appliances actually reduce the risk of nickel allergy following other exposure modalities? And why are intraoral reactions less frequent than extraoral reactions?

The Role of Orthodontically Derived Nickel

Epicutaneous retesting of 26 New York patients with a previously negative nickel reaction indicated that a conversion to a nickel-positive reaction after the insertion of nickel-containing orthodontic appliances took place in two cases. However, no intraoral or extraoral reactions were seen, and the lack of information from a similar testing approach among patients *without* orthodontic appliances made the observations inconclusive. Patch testing of about 700 Finnish adolescents showed no difference in the frequency of nickel sensitivity between previous orthodontic patients with fixed appliances and individuals who had received no orthodontic treatment. Other information points in the same direction: that the induction of nickel sensitivity by oral exposure to nickel-containing orthodontic appliances is not probable.

Actually, experimental and clinical studies indicate that oral exposure to nickel-containing alloys may reduce the chance of nickel sensitization by later exposure to the metal, *i.e.*, induce a certain *tolerance*. Oral exposure to nickel and chromium from alloys did not induce hypersensitivity in guinea pigs but rather suppressed the capacity to develop allergic responses to these metals. A large-scale European study on orthodontic patients tested in dermatology clinics indicated that treatment of young girls with archwires and metal brackets induced a partial *tolerance* for the T cell-mediated allergy induced by ear piercing that strongly partici-

pates in the development of nickel hypersensitivity. The prevalence of nickel hypersensitivity was higher in the group with pierced ears fitted with braces *after* ear piercing. The Finnish study referred to above showed similar results. Children who started orthodontic treatment before ear piercing had significantly *lower* prevalence of nickel hypersensitivity as compared to patients starting orthodontic treatment after ear piercing.

Reports on adverse effects after piercing of other body parts are concerned with infection problems and complications associated with the insertion. To our knowledge there have been no attempts to study the sensitization/tolerance relation between previous orthodontic treatment and forms of body piercing other than ear piercing.

Orthodontics and Previously Nickel-Sensitized Patients

As judged by studies of nickel allergy after ear piercing, intraoral exposure to nickel derived from orthodontic appliances apparently induces a partial tolerance toward other and later sensitization modalities. However, an orally induced nickel tolerance by orthodontic archwires and brackets does not eliminate the possibility of nickel sensitization by the extraoral parts of orthodontic appliances, similar to that from other nickel-containing objects with skin contact, nor does it prevent the expression of nickel allergy to orthodontic materials in previously sensitized patients. Case reports and epidemiological surveys indicate that adverse reactions occur more frequently extraorally than intraorally and that allergic reactions are difficult to distinguish from irritative reactions by clinical inspection alone. Generalized and serious allergic reactions to nickel-containing orthodontic appliances do occur. The reactions can be characterized by perianal dermatitis together with eczematous reactions of the knee and elbow flexures, generalized eczematous reactions on the trunk and extremities, general malaise, and eczemas of the wrists. These responses are observed following the insertion of nickel-containing orthodontic devices such as space retainers, arch wires, or molar bands in previously sensitized patients.

However, such cases do not appear at a predictable level in regular orthodontic practices. About one thousand Danish girls in active orthodontic treatment, presumably containing about 100 nickel-positive individuals, participated in a questionnaire study. Twenty showed oral rashes along with eczema, which was related to normal contact with metal objects as part of the treatment. Most reactions were attributed to causes such as mechanical injuries and acrylic allergy. Patch testing of the remaining patients, together with some patients reporting extraoral discomfort, showed the existence of nickel allergy in only one girl who exhibited aphthous ulcers. All other girls tested negative to nickel sulfate. However, the aphthae did not disappear upon removal of the orthodontic appliances. It was concluded that nickel allergy did not lead to an increased prevalence of allergic reactions following orthodontic treatment. Of the nine girls tested, six were classified as atopics.

These somewhat diverging observations illustrate the difficulties associated with the as-

essment of low-incidence reactions. A fair conclusion would be that nickel allergy following orthodontic treatment does occur in previously sensitized patients, but at a very low incidence. Extraoral reactions are significantly more frequent than intraoral reactions. Nickel sensitization of patients with intraoral orthodontic devices is highly improbable, whereas sensitization with extraoral devices cannot be excluded. Irritant reactions are sometimes difficult to distinguish from allergic reactions. And nickel may not always be the "culprit".

Published information on this subject ranges over several decades and includes observations that may have been misinterpreted or, by their nature, cannot be strictly scientifically verified. In addition, manufacturers of orthodontic appliances have adopted relevant information from materials research and development activities elsewhere to improve their commercial products by using more corrosion-resistant alloys and by coating metal surfaces. Previous information may therefore not fully reflect the actual situation today.

Occupational Implications

General Considerations

Every occupation carries some kind of health hazard connected with physical, chemical, ergonomic, and psychological factors. *Infectional* and *chemical* risk factors are specific for dental personnel. Orthodontic work includes repeated skin contact with biomaterials or their ingredients in preparing fixed or removable appliances, or in the insertion and clinical control of such appliances. Dusts associated with impression-taking and the production of models add to the occupational exposure to chemical risk factors. In addition, orthodontic personnel are exposed during work to liquids, such as disinfectants, detergents, and radiographic fluid, similar to those experienced by other dental personnel.

The repeated contact of operators with biomaterials and auxiliary materials entails a risk of developing allergies to orthodontically relevant biomaterials that may be greater than that of the patients. A bizarre aspect of this issue is the fact that infection control routines have initiated an increased use of gloves by

all dental personnel. However, latex and poly (vinyl chloride) (PVC) gloves do not prevent the penetration of liquid monomers or similar chemicals derived from resin-based materials, while the allergenic potential of latex *per se* represents an additional occupational risk factor. Recent reports show an increasing prevalence of latex allergy among dental personnel and students.

Observed Reactions

The Norwegian survey on adverse effects among orthodontists and their auxiliaries indicated that about half of the orthodontists had experienced some adverse occupation-related effects. The majority of reactions were hand and finger dermatoses, described in increasing severity as dryness, redness, itching, thickening, reduced tactile sensitivity, fissuring, soreness/desquamation, and pain. Most dermal reactions were of bearable severity and were associated with unspecified general conditions such as "dry air" and "ventilation problems," or

with soaps and detergents. Some 10% of the orthodontists had experienced dermal reactions related to work with composites and acrylics. For chairside assistants, model material-related work was more important. Both groups reported skin reactions to latex gloves. Nondermal respiratory reactions were associated with dusts from debonding procedures and vapors from cold-curing acrylics. Nickel reactions were not recorded in this survey. However, case reports and other surveys have revealed the occurrence of occupation-restricting nickel allergies, particularly among female auxiliary personnel in orthodontics. Reports from Sweden, Canada, and Italy have shown dermatological problems associated with resin-based bonding agents. Severe reactions near the fingertips were explained by a habit of using direct finger pressure during bonding procedures.

Safety Precautions

Basic considerations for adequate physical conditions are part of the planning process for every new dental clinic. Detailed safety guidelines have to reflect the activities taking place in each particular unit to reduce the possibility of dermal and respiratory exposure to chemical irritants and allergens. An orthodontic treatment unit may consist of clinical and laboratory facilities demanding different environmental

precautions: the safe handling of monomer/polymer chemicals in the production of removable appliances demands adequate overall ventilation and sufficient suction capabilities, combined with effective barrier equipment such as gloves and face masks. All grinding and polishing activities, the handling of powdered impression materials, and the production of models necessitate similar precautions.

Increased chairside safety for the operator includes obligatory reading of and *complying with* the instructions worked out by the manufacturer for safe handling of the materials that are used. For bonding materials, a “no-touch” technique is essential to avoid direct or glove-coated skin exposure. Some orthodontists consider that infection control does not require the use of gloves in a practice largely treating children and adolescents. They may have a point, in view of the irritant and allergenic problems associated with latex gloves. However, barrier equipment of this kind is an integral part of a modern hygienic regimen in dentistry, as well as in other health professions. In rare cases, even wet-strength paper masks may elicit irritant and allergic reactions because of residual chemicals such as formaldehyde associated with the production process. There is no consensus solution to the occupational problems related to barrier equipment, except to keep oneself updated on information from manufacturers and the health authorities.

Concluding Remarks

Orthodontics is a fascinating part of the dental profession that employs current biophysical principles and constantly seeks better and more effective biomaterials resources. Orthodontic treatment is generally uneventful as far as adverse effects associated with biomaterials are concerned. Exceptions are intraoral and extraoral irritant nuisances following orthodontic appliance contact, and, in rare cases, allergic reactions caused by components from resin-based bonding agents or removable appliances, and metal devices. The allergic problems associated with the orthodontic use of nickel-containing alloys for facebows, molar bands, brackets, and archwires have attracted the most attention, because nickel is a powerful general sensitizer. Information on

this subject has been adopted by the manufacturers of orthodontic materials, resulting in the production of “hypoallergenic” products such as plastic-coated metal devices, and plastic and ceramic brackets. Other products that should have improved biocompatibility, such as β -titanium archwires (Chapter 4) and the elastomeric chains and ligatures (Chapter 8), have also been developed. In addition, silver solders are increasingly being replaced by welding techniques. There are reasons to believe that this development has already had a positive influence on the prevalence of biomaterials-related adverse effects. In addition, the oral exposure to nickel may in fact induce a partial tolerance with regard to nickel sensitization.

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Appendix

Major Orthodontic Materials Companies

American Orthodontics

1714 Cambridge Avenue
Sheboygan, WI 53081
U.S.A.
Telephone +1-920-457-5051 or 800-766-3391*
Fax +1-920-457-1485
Internet www.americanortho.com

Class One Orthodontics

5064 50th Street
Lubbock, TX 79414
U.S.A.
Telephone +1-806-799-0608 or 800-343-5291
Fax +1-806-797-4604
Internet www.classoneortho.com

Den-Mat Corporation

2727 Skyway Drive
Santa Maria, CA 93455
U.S.A.
Telephone +1-805-922-8491 or 800-433-6628
Fax +1-805-922-6933
Internet www.denmat.com

Dentauram KG

J. P. Winkelstroeter KG
Turnstraße 31
75228 Ispringen
Germany
Telephone +49-7231 803-0
Fax +49-7231 803-295
Internet www.dentauram.de

Dentsply International

(Divisions include LD Caulk and De Trey)

570 West College Avenue
P.O. Box 872
York, PA 17405
U.S.A.
Telephone +1-717-845-7511 or 800-877-0200
Fax +1-717-849-4762
Internet www.dentsply.com

ESPE Dental AG

ESPE Platz
D-82229 Seefeld
Germany
Telephone +49-8152-700-0
Fax +49-8152-700-13-66
Internet www.espe.de

FORESTADENT Bernhard Förster GmbH

Westliche Karl-Friedrich-Straße 151
D-75171 Pforzheim
Germany
Telephone +49-7231-459-0
Fax +49-7231-459-102
Internet www.forestadent.de

GAC International

185 Oval Drive
Islandia, NY 11722
U.S.A.
Telephone +1-631-582-5700 or 800-645-5530
Fax +1-631-582-5704 or 800-422-2656
Internet www.gacintl.com

GC Corporation

76-1 Hasunuma-cho
Itabashi-ku
Tokyo 174-8585
Japan
Telephone +81-3-3558-5181
Fax +81-3-3966-1470
Internet www.gcdental.co.jp

G & H Wire Company

P.O. Box 248
Greenwood, IN 46142
U.S.A.
Telephone +1-317-346-6655 or 800-526-1026
Fax +1-317-346-6663
Internet www.ghwire.com

Gestenco International AB

P.O. Box 240 67
SE-400 22 Gothenburg
Sweden
Telephone +46 31-81 00 35
Fax +46 31-81 46 55
Internet www.gestenco.com

Lancer Orthodontics

253 Pawnee Street
San Marcos, CA 92069
U.S.A.
Telephone +1-760-744-5585 or 800-854-2896
Fax +1-760-744-5724
Internet www.lancerortho.com

* Telephone numbers with 800 prefix can only be used within the U.S.A.

Masel Enterprises

2701 Bartram Road
Bristol, PA 19007
U.S.A.
Telephone +1-215-785-1600 or 800-423-8227
Fax +1-215-785-1680
Internet www.maselortho.com

OREC Corporation

175-A9 Balboa Street
San Marcos, CA 92069
U.S.A.
Telephone +1-760-752-7630 or 800-624-5517
Fax +1-760-752-7636
Internet www.orecpmsi.com

Ormco (Includes Ormco/A-Company)

1717 West Collins Avenue
Orange, CA 92867
U.S.A.
Telephone +1-714-516-7400 or 800-854-1741
Fax +1-714-516-7543 or 800-317-6012
Internet www.ormco.com

**OSE Orthodontic Dental Supply
and Equipment Company**

7851 Airpark Road, Unit 202
Gaithersburg, MD 20879
U.S.A.
Telephone +1-301-869-3800 or 800-638-4003
Fax +1-301-869-3800
No internet site currently available

Ortho Organizers

1619 South Rancho Santa Fe Road
San Marcos, CA 92069
U.S.A.
Telephone +1-760-471-0206 or 800-547-2000
Fax +1-760-471-9549 or 800-888-7244
Internet www.orthoorganizers.com

Ortho Technology

8909 Regents Park Drive
Tampa, FL 33647
U.S.A.
Telephone +1-813-991-5896 or 800-999-3161
Fax +1-813-991-5986
Internet www.orthotechnology.com

Reliance Orthodontic Products

1540 West Thorndale Avenue
P.O. Box 678
Itasca, IL 60143
U.S.A.
Telephone +1-630-773-4009 or 800-323-4348
Fax +1-630-250-7704
Internet www.relianceorthodontics.com

RMO (Rocky Mountain Orthodontics)

650 West Colfax Avenue
Denver, CO 80204
U.S.A.
Telephone +1-303-592-8200 or 800-525-6375
Fax +1-303-592-8209
Internet www.rmortho.com

Saga Dental Supply A/S

P.O. Box 216
N-2202 Kongsvinger
Norway
Telephone +47-6-281-4898
Fax +47-6-281-9877
No internet site currently available

Shofu Inc.

11 Kamitakamatsu-cho
Fukuine, Higashiyama-ku
Kyoto 605-0983
Japan
Telephone +81-75-561-0411
Fax +81-75-561-0412
Internet www.shofu.co.jp

3M Dental Products

3M General Offices
Building 275-2SE-03
St. Paul, MN 55144
U.S.A.
Telephone +1-651-737-6501 or 800-364-3577
Fax +1-651-737-7117 or 800-713-6329
E-mail www.3m.com/dental

3M Unitek Corporation

3M Dental Products Division
2724 South Peck Road
Monrovia, CA 91016
U.S.A.
Telephone +1-626-574-4000 or 800-634-5300
Fax +1-626-574-4311 or 800-328-2360
Internet www.3m.com/unitek

TP Orthodontics

100 Center Plaza
La Porte, IN 46350
U.S.A.
Telephone +1-219-785-2591 or 800-348-8856
Fax +1-219-324-3029
Internet www.tporthodontics.com

Vivadent (Division of Ivoclar AG)

Bendererstraße 2
FL-9494 Schaan
Liechtenstein
Telephone +423-235 35 35
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Internet www.ivoclar.com

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